Microencapsulation Technologies for Corrosion Protective Coating Applications

Wenyan Li, Jerry Buhrow, and Scott Jolley
ESC-Team QNA
Corrosion Technology Laboratory
Kennedy Space Center, FL 32899

Luz Calle, Benjamin Pearman, and Xuejun Zhang
NASA, Kennedy Space Center
Corrosion Technology Laboratory
Kennedy Space Center, FL, 32899

ABSTRACT

Microencapsulation technologies for functional smart Coatings for autonomous corrosion control have been a research area of strong emphasis during the last decade. This work concerns the development of pH sensitive micro-containers (microparticles and microcapsules) for autonomous corrosion control. This paper presents an overview of the state-of-the-art in the field of microencapsulation for corrosion control applications, as well as the technical details of the pH sensitive microcontainer approach, such as selection criteria for corrosion indicators and corrosion inhibitors; the development and optimization of encapsulation methods; function evaluation before and after incorporation of the microcontainers into coatings; and further optimization to improve coating compatibility and performance.

Key words: Corrosion, Microencapsulation, microcapsule, microparticle, pH-sensitive microcapsule, smart coating, corrosion detection, corrosion indicator, corrosion sensing coating, corrosion inhibitor, corrosion control, corrosion protective coatings

INTRODUCTION

Microencapsulation is a commercially successful technology that has been used for controlled-release of active ingredients in pharmaceutical, agricultural, food, and paper industries.[1] In recent years, this technology has attracted increased interest from the coatings industry as well as the research community in the field of corrosion protective coatings. Due to their versatility and potential compatibility with organic coating systems, microcapsules containing active ingredients have been investigated for corrosion detection, inhibition, as well as self-healing of mechanical damage to coatings. The focus of this paper is on the use of microencapsulation technology to incorporate corrosion indicators and inhibitors into corrosion protective coatings. Self-healing coatings, obtained by incorporating encapsulated film-forming agents that are delivered when microcapsules rupture as a result of mechanical damage,[2,3,4]are beyond the scope of this paper.

This paper begins with a description of corrosion indication and sensing as a desirable function in a multifunctional smart corrosion protecting coating and the needs for an indicator delivery system for corrosion sensing coating development. It continues with corrosion inhibition, the challenges of introducing "green" (environmentally friendly) corrosion inhibitors into corrosion protective coatings, and the use of delivery systems for incorporation of corrosion inhibitors in coatings. A summary of the delivery systems reported in the literature is presented followed with detailed information on the pH-sensitive microcapsules and microparticles developed by the authors for incorporation of corrosion indicators and inhibitors into corrosion protective coatings.

DELIVERY SYSTEMS FOR CORROSION APPLICATIONS

Corrosion Sensing Coating: Needs for Delivery Systems

Early corrosion sensing is a desirable function in a smart coating for corrosion control applications. Corrosion is a costly problem that can lead to catastrophic structural failures. Thus, routine coating inspections are necessary for the maintenance of critical structures. It would be highly beneficial to detect corrosion at an early stage so that corrective action could be taken at a lower cost. Unfortunately, the usual visual inspections, which rely on the appearance of corrosion products, are not effective for early corrosion detection, especially when the corrosion damage occurs in hidden areas or when it happens in the form of localized corrosion, such as pitting and crevice corrosion. Many different sensors and techniques are being developed to detect corrosion. [5,6,7,8] Among these, corrosion sensing coatings are highly desired for corrosion detection, especially if they can generate a signal that can be detected during visual inspections by the naked eye or with the aid of a portable instrument at a stage that occurs significantly earlier than the appearance of the observable corrosion products.[9,10,11]

Earlier research on smart coatings,[8,9,10,] involved testing and evaluation of some promising corrosion indicators in solution, in gels, and even in coatings.[12,13,14] Subsequently, attempts were made to develop corrosion sensing coatings by incorporating corrosion indicators directly into commercially relevant coating formulas.[9,11]

Considering the wide range of materials that can potentially be used as corrosion indicators[12], the success of corrosion sensing coatings has been very limited. The main difficulties for incorporating these indicators into the targeted coating system can be attributed to the low solubility of the indicators and their poor compatibility with coating components. These difficulties can be addressed by incorporating the corrosion indicator into a delivery system. There are very few previous works in this area. Some of the early research, that used silica as a carrier system, partially solved the resin compatibility challenge but resulted in a reduction of indication sensitivity.[15] Cationic (e.g., montmorillonite) or anionic (e.g., hydrotalcite) nanoclays were studied as carriers for pH-responsive corrosion indicators, such as ionizable

dyes. These dye-doped clays were incorporated into coatings as corrosion indicators to detect localized corrosion through color change at the alkaline cathodic sites.[16]

Corrosion Inhibitors Delivery systems

Corrosion inhibitors have been used in corrosion protective coatings for a long time. In recent years, research to identify and incorporate new "green" corrosion inhibitors into corrosion protective coatings has been a growing area in the field of corrosion protection. The need for environmental friendly, yet effective corrosion inhibitors, is driven by the need to replace hexavalent chromium and lower volatile organic compounds (VOCs) in coatings. As a result of this research, new organic and inorganic corrosion inhibitors have been identified as candidate replacements for hexavalent chromium. However, these new corrosion inhibitors present challenges, as well as opportunities, in new corrosion protective coatings development. Organic inhibitors can be reactive, thus rendering them incompatible with coating systems, while inorganic corrosion inhibitors can be both reactive and highly water soluble. This high water solubility can cause several problems in coatings such as osmotic blistering and premature coating failure. An extensive review and a practical guide on inhibitor pigments were given by Sinko[17], who provided an insightful discussion on inhibitor solubility. These problems can potentially be addressed by a delivery system or media to protect these inhibitors from interacting with the coating and/or to reduce their dissolution rate.

Encapsulation is one of the approaches that have been used to reduce the solubility of the inhibitor. An example of this approach is the work of Yang and van Ooij[18] who have encapsulated soluble corrosion inhibitors, using plasma polymerization, to achieve a slow release of the inhibitor through a diffusion process. While this approach lowers the solubility of inhibitors in water, it is based on a mass-action governed release mechanism that is not a selective process for damage-induced activation. A similar effect was obtained by incorporating corrosion inhibitors into inorganic oxide nanoparticles and their porous sol-gel network structures were used as reservoirs for storage and prolonged release of inhibitors.[19,20,21,22,23] This approach addresses the high solubility as well as the compatibility issue of the inhibitor with resin systems. Besides inorganic nanoparticles, inorganic nano-containers are also used as a carrier system. For example, titanium dioxide (TiO_2), ceria (cerium oxide, CeO_2) and cerium molybdate ($Ce_2(MoO_4)_3$) nanocontainers were prepared through a 2-step process in which negatively charged polystyrene (PS) nanospheres were synthesized using emulsion polymerization and coated, via the sol-gel method, to form an oxide layer. This was followed by a thermal treatment that results in a hollow nanocontainer which in turn was filled with organic inhibitors, such as 2-mercaptobenzothiazole (2-MBT), 8-HQ, and paratoluenesulphonic acid (p-TSA).[24,25,26,27,28,29] Silica nanocapsules,[30,31] silica mesoporous spheres,[32,33] silica nanotubes,[34] and zeolite[35,36,37] have also been used as carrier systems for corrosion inhibitors. Another corrosion inhibitor delivery system involves the use of ion exchange corrosion-inhibiting pigments. Anion exchanging hydrotalcites,[38,39,40,41,42,43,44,45,46,47,48] as well as cation exchanging bentonites,[41,48] have been studied. So far, anion exchanging hydrotalcite-like double layer hydroxides (DLHs) have been found to be more effective as corrosion inhibitors. For instance, it was demonstrated that hydrotalcite, rehydrated in the presence of inhibitor anions, such as phosphate and chromate, provides excellent inhibition for filiform corrosion. The anion exchange pigments, when formulated into paint, work to limit filiform corrosion by lowering the chloride activity through ion exchange and by buffering the acidic pH of the anodic head of the filiform. Another advantage of ion-exchange pigments, at least theoretically, is that they can reduce blistering by eliminating inhibitor leaching. Organic capsules and containers are also used as corrosion inhibitor delivery systems. [49,50,51,52,53,54,55]

While some of the above methods constitute an improvement from simple inhibitor release by leaching, release mechanisms that are triggered by the electrochemical environment directly related to corrosion are more desirable and have become an area of intense research in recent years. Polyelectrolyte layers have been used to provide pH-controlled release in various systems, including sandwich-like layers on metal substrates, with inhibitors as one of the layers, [56,57,58] or polyelectrolyte-modified silica (SiO_2)

nanoparticles[59] and nanocontainers,[60] polyelectrolyte-modified halloysite nanotubes,[61,62] and polyelectrolyte capsules.[62]

In summary, research on delivery systems for corrosion inhibitors has been significantly more active than that on delivery systems for corrosion indicators. Among the inorganic systems, the aluminum (Al)/zinc (Zn) LDH system shows promise in filiform corrosion (FFC) inhibition. This is credited to its multifunctional performance that involves removing chloride ions (Cl^-) while releasing an anionic inhibitor. Its basic pH also neutralizes acid, which can be beneficial for Al or steel substrates. The only apparent shortcoming is its limitation as an anion inhibitor carrier. Sol-gel inorganic oxide systems are natural choices for sol-gel based pretreatment coatings. However, their main release mechanism through leaching may be a concern for some coating systems. While inorganic containers synthesized from a template can be used to deliver a wide range of core contents, their tendency to leach could cause blistering when used to deliver inhibitors with higher solubility and also limit their ability to improve inhibitor/resin compatibility. Microcapsules and microparticles from below 100 nm to tens of microns are among the delivery systems that have been synthesized and tested. Some of these systems exhibit corrosion-controlled release properties. So far, the challenges encountered in organic systems seem to be paint formulation compatibility and the suitability for forming pigment grade additives.

The development of corrosion inhibitor delivery systems must take into account the solubility of the inhibitor, the compatibility between the carrier and the inhibitor, the compatibility between the carrier and the coating resin systems, as well as the water permeability of the cured coatings. It is likely that an inhibitor delivery system that works well in a given coating system on a given substrate might not work well on another coating system or for another substrate. It is very unlikely that a single delivery system can be developed for all corrosion inhibitors, all coatings, and all substrates.

PH SENSITIVE MICRO-CONTAINERS FOR SMART COATINGS APPLICATION

Smart Coating Concept

The authors have developed pH-triggered release microcapsules for early corrosion detection and corrosion protection.[63,64,65] The microcapsule wall is designed to break down and release the encapsulated contents in response to the pH at the cathodic site of localized corrosion. 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 1). 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.[12]

The pH-controlled release microcapsule design has, in addition to all the advantages of the microcapsule design, the true controlled-release function for corrosion applications. While most 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.
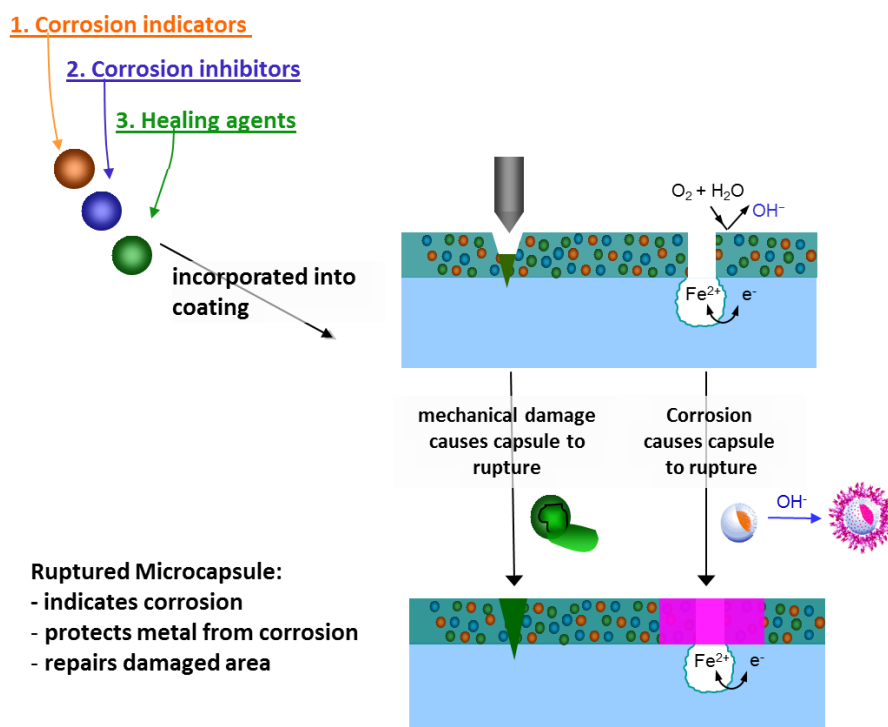
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Figure 1. Conceptual illustration of smart coating with pH sensitive microcapsules for corrosion protection applications.

Microencapsulation Process Development

As mentioned earlier, microencapsulation technologies have been widely used to develop delivery systems in various industries. There are common as well as unique challenges for each different application. In the case of microencapsulation of corrosion indicators and inhibitors for smart corrosion protective coatings, like it is the case in other applications, it is important that the encapsulation process does not have detrimental effects on the active ingredient. The unique challenge, specific to corrosion protection coatings, is obtaining microcapsules and microparticles as coating pigment-grade products. This requires: mechanical strength to survive the coating production process, chemical compatibility with a wide range of resin systems, small size, narrow size distribution, long shelf life, easiness to handle, preferably available as a free flowing powder, and easy dispersion with minimal grinding. Another important consideration is the scalability of the microencapsulation process. With these goals in mind, several microcapsule and microparticle formulas have been developed to incorporate corrosion indicators and inhibitors into corrosion protective coatings. The formulas developed so far include: pH-sensitive oil-core or hydrophobic-core microcapsules, water-core or hydrophilic-core microcapsules, and microparticles.

As shown in Figure 2, there are several steps involved in the development and optimization of microcapsules and microparticles for corrosion indicators and inhibitors. These include: selection of encapsulation media, selection of encapsulation method, selection of microcapsule wall materials, and microcapsule/microparticle testing and optimization. The solubility or ability to disperse in a selected media of the core materials determines their suitability for encapsulation into oil-core microcapsules, water-core microcapsules, or microparticles. Several of the encapsulation (polymerization) methods that are commonly used to form microcapsules or microparticles include: interfacial polymerization, in situ polymerization, emulsion polymerization, and solvent evaporation. A wide range of wall materials can be

used to obtain the desired wall properties, such as controlled release rate, mechanical strength, and thermal stabilities, of the microcapsules. After the initial selection is made, trial tests are conducted and the results used to optimize the encapsulation process, microcapsule size, size distribution, wall properties, and release properties.
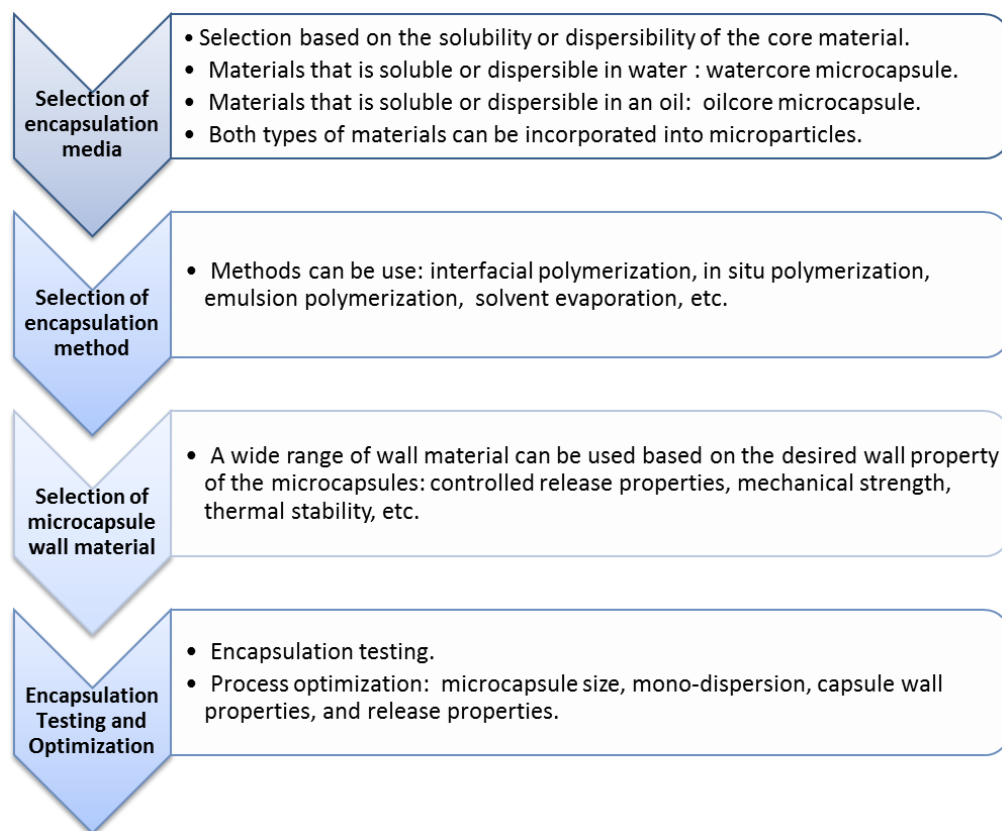
Selection of encapsulation media
- Selection based on the solubility or dispersibility of the core material.
- Materials that is soluble or dispersible in water : watercore microcapsule.
- Materials that is soluble or dispersible in an oil: oilcore microcapsule.
- Both types of materials can be incorporated into microparticles.

Selection of encapsulation method
- Methods can be use: interfacial polymerization, in situ polymerization, emulsion polymerization, solvent evaporation, etc.

Selection of microcapsule wall material
- A wide range of wall material can be used based on the desired wall property of the microcapsules: controlled release properties, mechanical strength, thermal stability, etc.

Encapsulation Testing and Optimization
- Encapsulation testing.
- Process optimization: microcapsule size, mono-dispersion, capsule wall properties, and release properties.

Figure 2. The development of the encapsulation process.

The experimental details of the encapsulation processes are presented by the authors elsewhere,[63,66, 67,68] this paper highlights the technical approaches that are unique to develop pigment-graded delivery systems for corrosion protective coatings, such as selection criteria for corrosion indicators and corrosion inhibitors, the development and optimization of encapsulation methods, function evaluation before and after incorporation of the micro-containers into coatings, and further optimization to improve coating compatibility and performance.

Selection of Corrosion Indicators and Inhibitors

Selection of Corrosion Indicators

The detection of corrosion can be achieved either through a visible color change[69,70,71] or a fluorescence change.[72,73,74,75] While observation of a visible color change can be convenient for traditional visual corrosion inspections, fluorescent compounds provide much greater sensitivity, and can be more readily detected by optical equipment.

Due to the electrochemical nature of the corrosion process, three types of color or fluorescent indicators can be used for corrosion: redox indicators for the electron transfer, pH indicators to detect the pH

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changes, and ion indicators for metal ions. While all three types would be effective for early corrosion detection, indicators that target cathodic reaction would be more effective to detect hidden corrosion, in cases where crevice corrosion is involved. For a cathodic indicator, it is preferable that the color or fluorescence 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 indication. Phenolphthalein and fluorescein are good examples of cathodic indicators.

<u>Selection of Corrosion Inhibitors</u>

Corrosion inhibitors belong to a large and growing family of chemical compounds, both inorganic and organic in nature. Encapsulation can be used to control the release properties of the inhibitors and increase their coating compatibility. Many inhibitors can benefit from this process, such as various inorganic inhibitors, due to their high solubility and leaching rates, and organic inhibitors, due to their reactivity with the resin systems.

Development of Encapsulation Methods

Several microcapsule/microparticle formulas have been developed to incorporate the corrosion indication and inhibition functions into coating systems: oil-core microcapsule, water-core microcapsule, and microparticles. Figure 3 shows some example scanning electron microscopy (SEM) images of these delivery systems containing corrosion indicators.
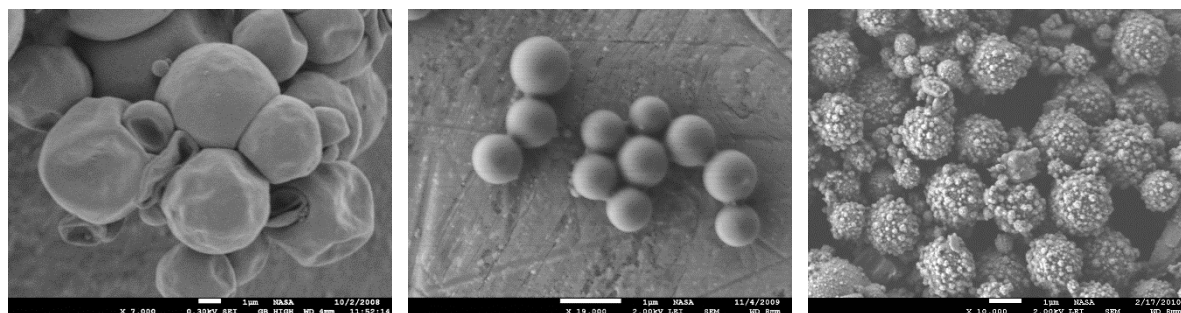

Figure 3. SEM images of oil-core microcapsules (left), water-core microcapsules (middle), and microparticles (right) containing corrosion indictor phenolphthalein.

Both oil-core and water-core microcapsules can be synthesized through interfacial or in situ polymerization process. A typical oil-core microcapsule formation process is shown in Figure 4, where the capsule wall forms by the polymerization process at the oil/water interface after an oil-in-water emulsion is formed. The water-core microcapsule formation process is similar, with the dispersed and continuous phases reversed. While water-core microcapsule is ideal for encapsulating water soluble or water dispersible core content and oil-core microcapsule ideal for encapsulating oil soluble or oil dispersible core content, it is possible to incorporate an active ingredient with limited solubility into the capsule core with the aid of a co-solvent, such as ethanol, as shown in the cases of oil-core and water-core microcapsules containing phenolphthalein.
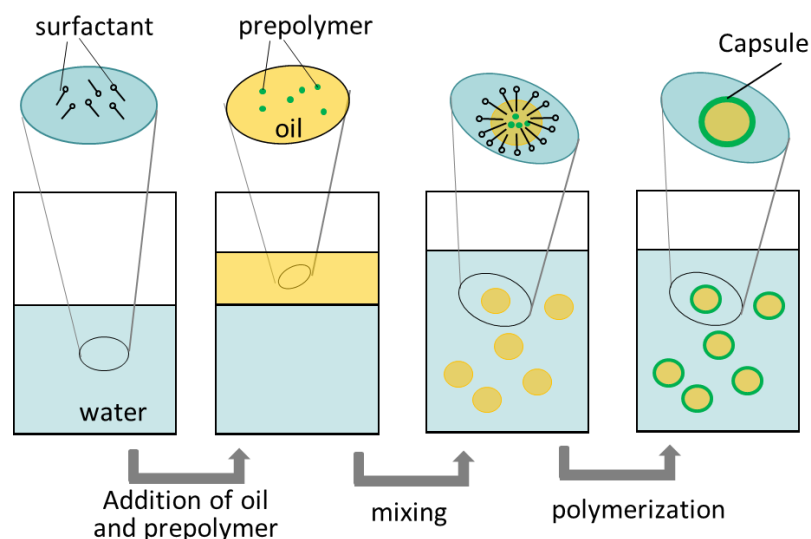
Figure 4. Interfacial polymerization process for making oil-core microcapsules.

The microparticles are synthesized through a different process. A representative inhibitor microparticle synthesis process is shown Figure 5. The two phases involved are the water phase and the solvent phase. The water phase contains the pre-polymer for particle formation and the surfactants. The solvent phase contains a water-miscible solvent with an active ingredient. The solvent phase with the active ingredient is then added to the water phase. This process allows the active ingredient to be incorporated into the particle rather than being dissolved into the water. While the process is not completely understood, it involves a somewhat spontaneous emulsification process, by which the active ingredient (with some solvent) is dispersed into droplets. The polymerization reaction then occurs at the interfaces of these droplets which cause the active ingredient to be incorporated into particles before being dissolved or dispersed in the water. Surfactants are used to control size and maintain particle distribution of the particle formation.
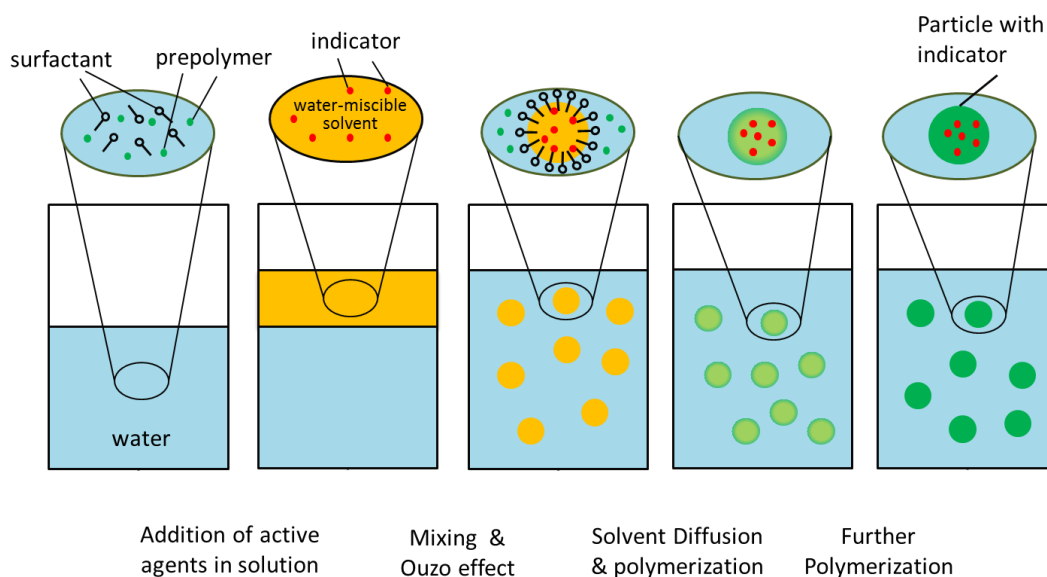

Figure 5. Schematic representation of the particle formation process.

Evaluation and Optimization of Encapsulation Methods

After the initial encapsulation formulations are developed, it usually takes several steps of optimization before the encapsulated indicator/inhibitors can be successfully incorporated into a coating formulation. Some of the optimization process steps are common to all encapsulation process, such as improvement in size distribution and capsule wall strength, while others are unique for corrosion detecting and protective coating applications which are the focus of the following section.

Function testing of encapsulated indicators and Inhibitors

All of the microcontainers containing corrosion indicators (shown in Figure 3) were tested for their 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 indicator 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 indicator.

The corrosion protective properties of the encapsulated inhibitors are tested before and after they are incorporated into coating formulations. Weight loss and electrochemical methods are used to test the encapsulated inhibitor suspended in salt solution. Due to the lack of direct correlation between the performance of the inhibitors and that of the inhibitor containing coatings, these results are not relied on as screening methods. They are used instead to provide insights for the optimization of the encapsulation process. Standard salt fog testing (ASTM B117)[76] and atmospheric exposure have been used for inhibitor evaluation in coatings. The limitation of B117 is well recognized, but a standard test is needed for quick evaluation and screening.

Releasing Properties

Control of the inhibitor release is one of the essential functions of the encapsulated inhibitors. Different release rates are likely needed for different inhibitors with various inhibition mechanisms, for different metal substrates, in different coating systems, under different exposure conditions. The ability to adjust and adopt is one of the advantages of the encapsulation process.

Due to the complexity of the coated metal corrosion process, there are no established guidelines for target release rates of various corrosion inhibitors. The optimized release rate is often identified through trials, but for experienced paint formulators, there are tell-tale signs during coating tests. Too much inhibitor usually causes blistering or other resin or formulation incompatibility, while lack of protection indicates not enough inhibitors.

Different techniques can be used to track different inhibitors and measure their release rates; conductivity might be sufficient for ionic inhibitors, while UV-Visible HPLC (high performance liquid chromatography) might be needed for some organic inhibitors.

Figure 6 shows some examples of encapsulated inhibitors. On the left, the release rates of three samples were compared through conductivity testing: (1) a watercore microcapsule with water soluble inorganic inhibitor, (2) a commercial pigment of inorganic inhibitor, and (3) the commercial pigment encapsulated with pH sensitive polymer. Note that encapsulated water soluble inhibitor releases much faster release, while encapsulating a pigment slows down its release. On the right, the release rates of three microparticles containing organic inhibitor 2-Mercaptobenzothiazole (2-MBT) were compared using UV-Visible HPLC method, the different release rates are achieved by varying encapsulation process.
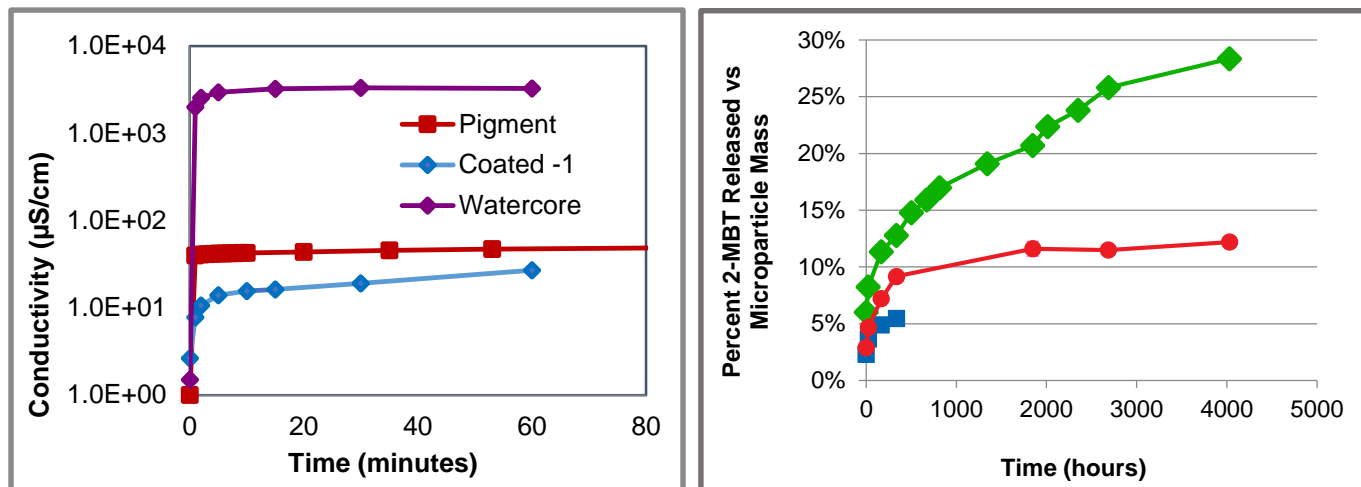
Figure 6. Release properties of different encapsulated inhibitors measured by conductivity method (left) and HPLC UV-Vis method (right).

Coating compatibilities

Encapsulated inhibitors are expected to behave like pigment-graded materials, with small and homogenous sizes, easy to be dispersed and incorporated into paint formulations. A common problem for microcapsules is their tendency to form clusters in coating resins. This is usually caused by one of the following reasons: (1) the capsule surface is not free of excess surfactants, oil or water from the encapsulation process; (2) the wall forming reaction is not completed, and there are reactive functional groups on the outside of the containers that caused them to fuse together; (3) high surface tension between the container surfaces and the resin systems. Complete curing and cleaning of the microcontainers can address the first two problems, but the third one might require the aid of a dispersing agent.

While wet capsules or particles can be used in some coating formulations, a dried powder is usually easier to handle. Both freeze drying and spray drying can provide free flowing powder, but the spray drying process does provide additional curing for the capsule/particle surface.

Compatibilities with the coating application process

The coating application process often involves high shear during pigment grinding and coating spraying. Concerns of the mechanical strength of the delivery systems and their survivability during coating application process are valid but perhaps often overstressed. If the microcontainers have small sizes, have been properly cleaned and cured, and have no dispersing issues, it is likely they will survive the application process without structural damage or premature release.

Thermal stability of the delivery system is important if the coating needs to be cured at elevated temperature. It is also desirable even if the coating can be cured at room temperature, as good thermal stability often indicates long shelf life.

Coating protection performance improvement

Encapsulation methods provide delivery systems for various corrosion inhibitors, and they can be effective additions to the existing paint formulation techniques when properly applied. As mentioned

earlier, some water soluble inhibitors can be encapsulated and incorporated into coating formulations to provide quick response when a coating is damaged, without causing blistering in the coating. Some effective organic inhibitors suffer high reactivity with important coating resins while their encapsulated forms have improved coating compatibilities and maintain their effectiveness as corrosion inhibitors. Figure 7 shows SEM images of water-core microcapsules of Na_2MoO_4, a water soluble inorganic inhibitor, and microparticles with 2-MBT, an organic inhibitor.
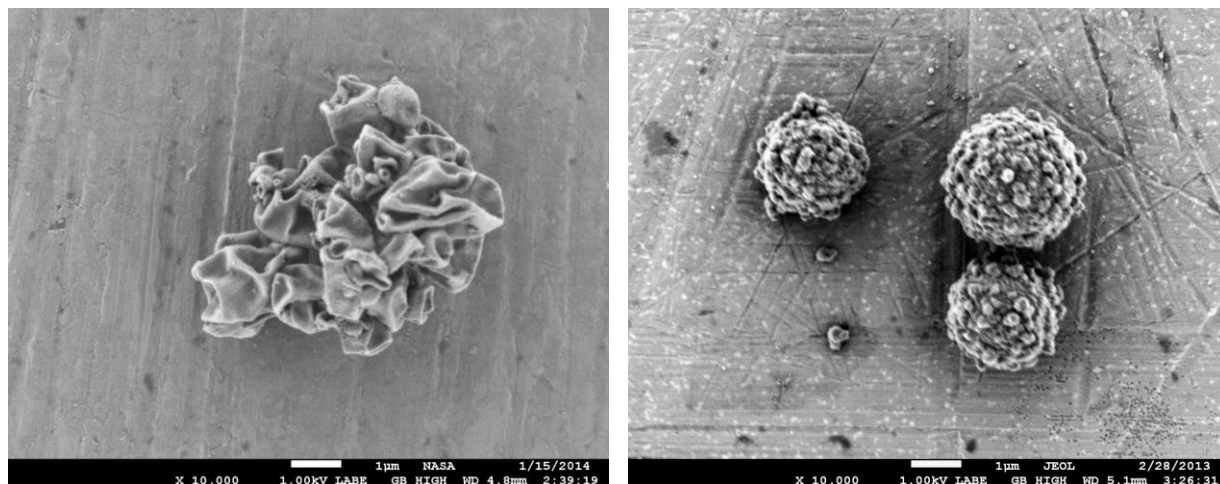

Figure 7. SEM images of encapsulated corrosion inhibitors: water-core microcapsules with Na_2MoO_4, and microparticles with 2-MBT.

Another not-so-obvious benefit of encapsulation can be obtained by encapsulating inhibitor that is already pigment graded material for extended protection through prolonged release. Figure 8 shows SEM images of a commercial inhibitor before and after being encapsulated with pH sensitive polymer.
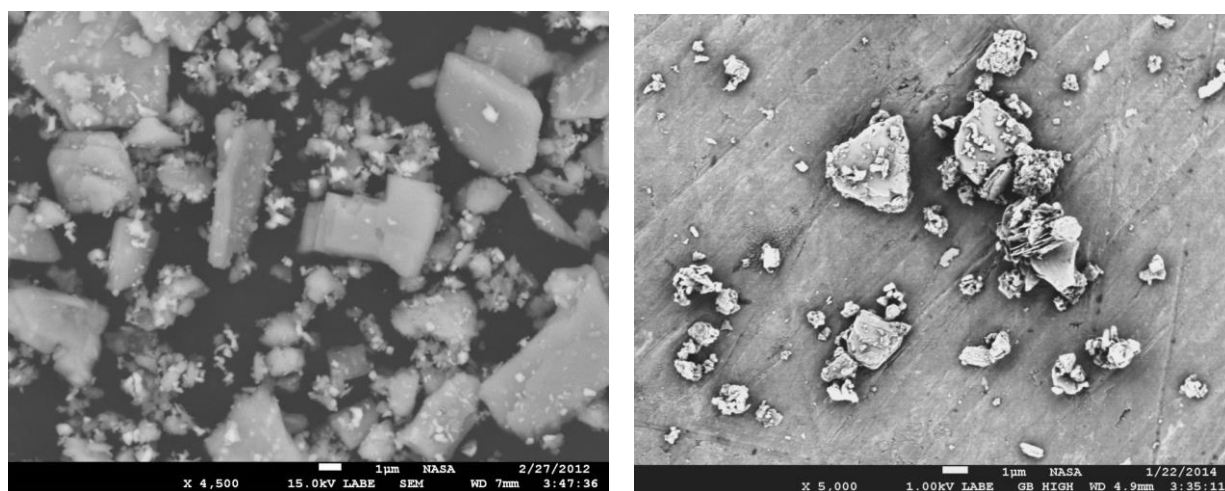

Figure 8. SEM images of corrosion inhibitor pigments before (left) and after being encapsulated with pH sensitive polymer.

SUMMARY

Microencapsulation has attracted increased interest from the corrosion protective coating community. The development of inhibitor delivery systems for corrosion inhibitors has been a contested research area while there are clear needs for indicator delivery systems for corrosion sensing applications. A summary of the delivery systems reported in the literature is presented followed with detailed information on the pH-sensitive microcapsules and microparticles developed by the authors for incorporation of corrosion indicators and inhibitors into corrosion protective coatings, such as selection criteria for corrosion indicators and corrosion inhibitors; the development and optimization of encapsulation methods; function evaluation before and after incorporation of the microcontainers into coatings; and further optimization to improve coating compatibility and performance.

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