Corrosion-Activated Micro-Containers for Environmentally Friendly Corrosion Protective Coatings

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The need to replace hexavalent chromium for environmental compliance in corrosion control, has motivated intense research and development efforts to focus on alternate corrosion inhibitors and coating formulations to incorporate these new inhibitors. As a result, new and old corrosion inhibitors are being tested and evaluated for corrosion protective coating applications. As challenging as it is to match the corrosion inhibition effectiveness of hexavalent chromium, it has been equally challenging to develop a pigment-grade product that is compatible with coating formulations. Organic inhibitors can be reactive, thus rendering them incompatible with coating systems, while inorganic corrosion inhibitors can be both reactive and highly soluble in water. High water solubility can cause several problems in coatings such as lowering the barrier properties of the coating, possible spontaneous leakage, and uncontrolled release of the corrosion inhibitor, osmotic blistering, and premature coating failure.[1] These problems can potentially be addressed by a delivery system or media to prevent these inhibitors from interacting adversely with the coating and/or to control their delivery rate. While controlled delivery concepts and systems have been used in pharmaceutical and agricultural applications for many years, their use in corrosion protection is a more recent area of research interest.

Figure 1 shows a conceptual illustration of how encapsulation into pH sensitive microcapsules can be used to deliver corrosion indicators, corrosion inhibitors, and self-healing agents when the micro containers are incorporated into a coating. Microcapsules are hollow micro particles composed of a solid polymer shell surrounding a core-forming space available to entrap substances or mixtures. The core contents remains in the microcapsule until its delivery is triggered by a change that accompanies the onset of corrosion such as the pH increase that occurs in the cathodic area. The microcapsule wall was designed to break down under basic pH conditions.

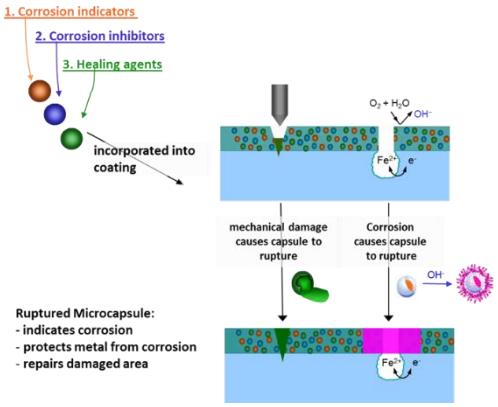

Figure 1. Conceptual illustration of a smart coating with pH sensitive microcapsules for corrosion control management.

Experimental results obtained with microcapsules revealed some limitations that lead to the development of pH sensitive micro particles. In a micro particle, the active agent is interspersed throughout a polymer matrix, instead of being encapsulated in an interior compartment/core inside a polymer wall/shell. Micro particles have some advantages over microcapsules such as: incorporation of a higher concentration of the active agent that is not limited by its solubility; a polymer matrix structure that can be tailored to release the active corrosion management ingredient at different rates rather than all at once; the versatility to use a layering system in which different layers release the inhibitor at different rates; and a greater mechanical strength than that of the microcapsules. These properties allow the micro particle to be customized to meet the requirements of the application. The authors have developed micro particles with matrixes of pH sensitive polymers (organic and inorganic), and with a hybrid matrix in which the inorganic polymer is coated with an organic polymer. As shown in Figure 2, there are several steps involved in the development and optimization of micro-containers (microcapsules and micro-particles) for corrosion management agents such as indicators and inhibitors. These include: selection of encapsulation media, selection of encapsulation method, selection of shell or matrix materials, and micro-container properties testing and optimization. The solubility or ability to disperse the core materials in a selected media determines their suitability for encapsulation into oil-core microcapsules, water-core microcapsules, or micro-particles. Several of the encapsulation (polymerization) methods that are commonly used to form microcapsules or micro particles include: interfacial polymerization, *in situ* polymerization, and emulsion polymerization. A wide range of wall materials can be used to obtain the desired wall or matrix properties, such as controlled release rate, mechanical strength, and thermal stability, of the micro particles. After the initial selection is made, trial tests are conducted and the results are used to optimize the encapsulation process, microcapsule size, size distribution, wall properties, and release properties. The experimental details concerning the development of pH-sensitive micro containers have been previously reported.[2-7]

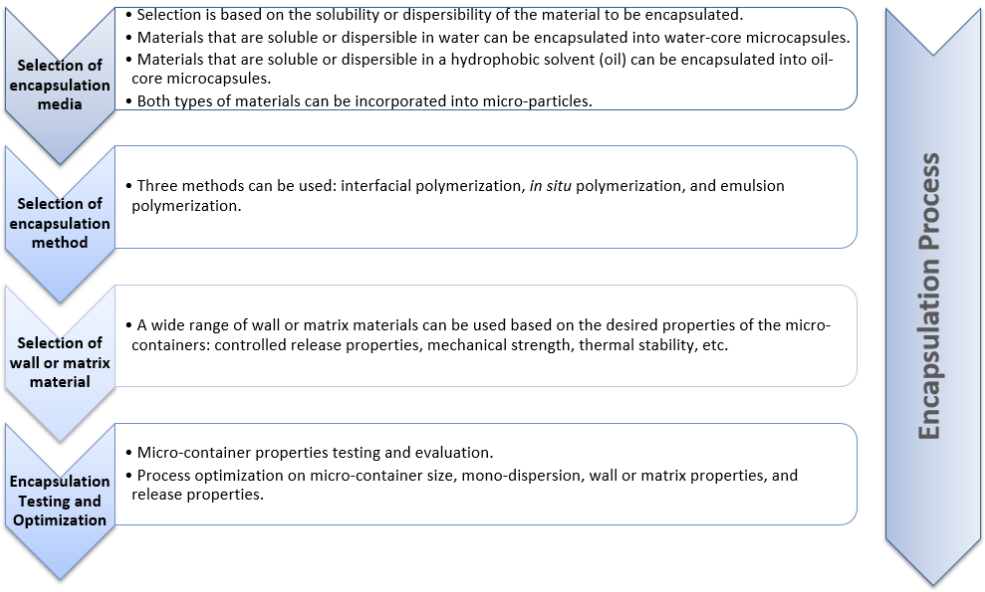

Figure 2. Development of the encapsulation process.

Microcapsules for the delivery of film-forming compounds to repair mechanical damage to a coating have also been developed and tested.[6] Recent research and development efforts have been concentrated on improving coating compatibility and synthesis procedure scalability, with a targeted goal of obtaining easily dispersible pigment-grade type microencapsulated materials.

Figure 3 shows SEM images of three types of corrosion-activated micro containers: hydrophobic-core microcapsules, hydrophilic-core microcapsules, and pH-sensitive micro particles.

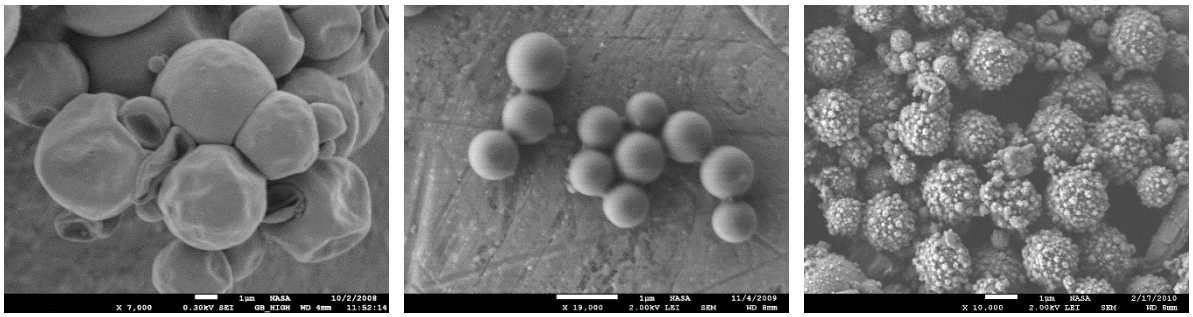

Figure 3. SEM images of hydrophobic-core microcapsules (left), hydrophilic-core microcapsules (middle), and micro particles (right) loaded with phenolphthalein.

Both hydrophobic-core and hydrophilic-core microcapsules can be synthesized through interfacial or *in situ* polymerization. A typical hydrophobic-core microcapsule synthesis procedure is illustrated in Figure 4, where the capsule wall forms by the polymerization reaction at the oil/water interface after an oil-in-water emulsion is formed.

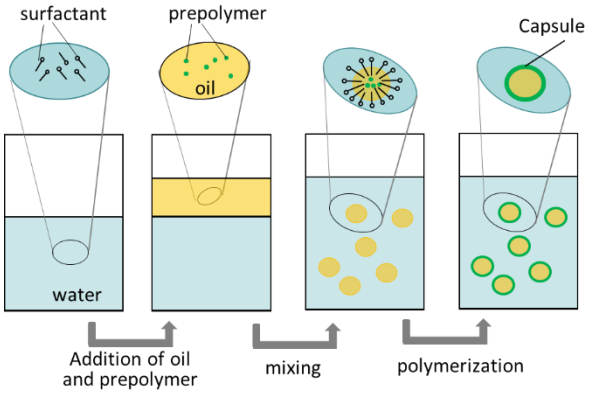

Figure 4. Interfacial polymerization procedure for making hydrophobic-core microcapsules.

The hydrophilic-core microcapsule synthesis procedure is similar to that of the hydrophobic-core microcapsule, with the dispersed and continuous phases reversed. While hydrophilic-core microcapsules are ideal for encapsulating water soluble or water dispersible core content and hydrophobic-core microcapsules are ideal for encapsulating oil soluble or oil (hydrophobic solvent) dispersible core content, it is possible to incorporate an active ingredient with limited water solubility, such as the pH indicator phenolphthalein, into hydrophobic-core and hydrophilic-core microcapsules. All the micro containers shown in Figure 3 were tested for their pH and corrosion indica-

tion functions through a color change in solution, in gel, and in paint. As it was anticipated, the micro particles achieved the most intense color change and proved to be more suitable than microcapsules to incorporate a higher concentration of phenolphthalein.

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

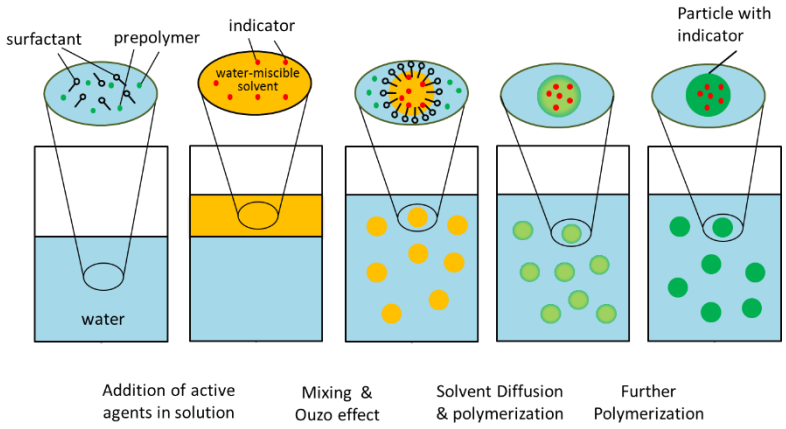

Figure 5. Schematic representation of the micro particle formation process.

One of the desired properties of encapsulated inhibitors is a controllable release rate. Different release rates are likely to be needed depending on the inhibitor, the mechanism by which the inhibitor protects the substrate, the metal substrate, the coating system, and the actual service conditions in which the coating will be used.

Due to the complexity of the corrosion process in a coated metal, there are no established guidelines for target release rates of corrosion inhibitors. The optimized release rate is often identified experimentally. The fast release of too much inhibitor usually causes blistering or other resin or formulation incompatibility problems, while lack of corrosion protection indicates that not enough inhibitor was released. Different techniques can be used to track different inhibitors and measure their release rates: conductivity measurements might be suitable for ionic inhibitors, while UV-Visible HPLC (high performance liquid chromatography) is suitable for some organic inhibitors.

Figure 6 shows examples of results obtained on the release properties of encapsulated inhibitors. The graph on the left shows the release rates of three inhibitor samples: (1) a hydrophilic core microcapsule (water core) with a water soluble inorganic inhibitor, (2) a commercial pigment of inorganic inhibitor (Pigment), and (3) the commercial pigment encapsulated with a pH sensitive polymer (Coated-1). The encapsulated water

soluble inhibitor was released at the highest rate while encapsulation slowed down the delivery rate of the commercial pigment. The graph on the right, shows three different release rates of the organic inhibitor 2-Mercaptobenzothiazole (2-MBT) from micro particles in which the encapsulation procedure was modified to control the rate of release.

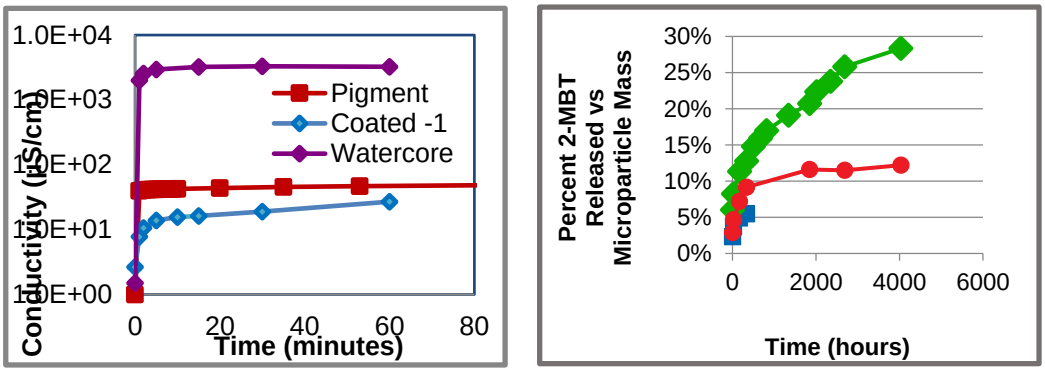

Figure 6. Release properties of different encapsulated inhibitors measured by the conductivity method (left) and by the HPLC UV-Vis method (right).

The authors have developed corrosion-activated micro containers for the incorporation of corrosion indicators and inhibitors into corrosion protective coatings. This work has led to the conclusion that the encapsulation process has to be tailored to the active ingredient, to the coating, to the substrate, and to the actual service conditions of the coating. It has also been concluded that the release rate is an important property that needs to be tailored to the specific application and that long-term corrosion protection may require the incorporation of more than one encapsulated corrosion inhibitor with different rates of release for immediate and long-term corrosion protection. It is important to realize that progress in this area also relies strongly on the understanding of the mechanism by which inhibitors protect metals from corrosion.

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