

Environmentally Friendly Coating Technology For Autonomous Corrosion Control

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This work concerns the development of environmentally friendly encapsulation technology, specifically designed to incorporate corrosion indicators, inhibitors, and self-healing agents into a coating, in such a way that the delivery of the indicators and inhibitors is triggered by the corrosion process, and the delivery of self-healing agents is triggered by mechanical damage to the coating. Encapsulation of the active corrosion-control ingredients allows the incorporation of desired autonomous corrosion-control functions such as: early corrosion detection, hidden corrosion detection, corrosion inhibition, and self-healing of mechanical damage into a coating. The technology offers the versatility needed to include one or several corrosion-control functions into the same coating.

The development of the encapsulation technology has progressed from the initial proof-of-concept work, in which a corrosion indicator was encapsulated into an oil-core (hydrophobic) microcapsule and shown to be delivered autonomously, under simulated corrosion conditions, to a sophisticated portfolio of micro carriers (organic, inorganic, and hybrid) that can be used to deliver a wide range of active corrosion ingredients at a rate that can be adjusted to offer immediate as well as long-term corrosion control. The micro carriers have been incorporated into different coating formulas to test and optimize the autonomous corrosion detection, inhibition, and self-healing functions of the coatings. This article provides an overview of progress to date and highlights recent technical developments, such as improved corrosion detection sensitivity, inhibitor test results in various types of coatings, and highly effective self-healing coatings based on green chemistry.



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INTRODUCTION

The development of cost-effective, environment-friendly, corrosion-resistant materials and coatings has been one of the grand challenges in corrosion research, as it was officially acknowledged in the United States by the Committee on Research Opportunities in Corrosion Science and Engineering of the National Research Council.¹ This challenge has been one of the main drivers in the development of new technologies to find a replacement for hexavalent chromium-containing coatings, which pose a health and environmental hazard and are scheduled to be banned under the Registration, Evaluation and Authorization of Chemicals (REACH)—the European Union's chemical safety regulation—by 2017.

The need for environmental compliance in corrosion control has motivated intense research and development efforts to focus on alternate corrosion inhibitors and coating formulations to incorporate them. As a result, new and old corrosion inhibitors have been tested and evaluated for corrosion-protective coating applications. As challenging as it is to find a corrosion inhibitor that comes close to hexavalent chromium in corrosion inhibition efficiency, it has been equally challenging to develop a pigment-grade product that is compatible with coating formulations. Achieving coating compatibility can be a challenge with a new corrosion inhibitor when: (1) the solubility of the inhibitor is too high, (2) the inhibitor is too reactive, and thus not stable in the presence of other coating components, and (3) has other negative effects on the coating formulation that affect storage, application, curing or use, and emulsion stability. To overcome the coating compatibility challenge, the development of an inhibitor delivery system is often necessary. While controlled delivery concepts and systems have been used in pharmaceutical and agricultural applications for many years, their use for

corrosion control applications is a more recent development.²

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 system, 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

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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.

Early corrosion sensing and detecting coatings have been an area of research interest due, at least in part, to some corrosion-related catastrophic failures such as those involving aged aircraft.³⁻⁵ The failures often were the result of the sudden fracture of high strength aluminum alloys caused by localized corrosion, which can be easily overlooked using the traditional and most often used visual inspection techniques. Other incidents involve new coating products that are often developed to address environmental compliance and economic factors. These coatings sometimes fail earlier than expected due to the fact that there is no correlation between the specified accelerated and/or laboratory corrosion tests used to evaluate them and actual field performance. These incidents highlight the need for early corrosion detection

technology, especially for corrosion in recessed/hidden areas. Besides safety concerns, another obvious benefit for early corrosion detection and hidden corrosion detection is economic impact. When detected early, coating and corrosion damage require minor repair at a lower cost compared to the high expense of a major structural overhaul. The cost difference can be significant. While damage detection sensors and tools are being developed to aid corrosion inspection, a protective coating with an integrated corrosion-sensing function is highly desirable. Earlier research in corrosion-sensing paints involved the incorporation of corrosion-sensing compounds directly into the paints.⁶⁻⁹ More recent efforts involved corrosion indicators with higher detection sensitivity^{10,11} and different delivery systems to overcome coating incompatibilities.^{12,13}

Self-healing materials have been a recent and rapidly growing field of research. The initial research that targeted composites¹⁴ has subsequently spread into other areas.¹⁵⁻²¹ Research in self-healing polymer coatings, as a subset of self-healing polymers, includes two approaches: built-in structures that provide healing functions^{11,19} and polymer chemistries that provide intrinsic self-healing.²⁰⁻²²

Our research on smart coatings for corrosion management applications has evolved from the earlier efforts to develop pH-sensitive microcapsules²⁰⁻²³ to incorporate the functions of indication, inhibition, and self-healing into a smart coating, to more recent efforts to tailor and fine-tune the microencapsulation system for each function. New delivery systems, such as pH-sensitive organic micro-particle formulations for indicators and inhibitors, elongated microcapsules for self-healing, as well as new self-healing chemistries, inorganic, and hybrid (inorganic/organic) delivery systems are currently under development, evaluation, and optimization. These newer delivery systems

are being developed as pigment-grade materials to be easily incorporated into paint formulations that are targeted towards several commercial applications.

MICROENCAPSULATION PROCESS DEVELOPMENT

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 micro-particles as a coating pigment-grade product. 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, ease of handling, 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 micro-particle 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 micro-particles (organic, inorganic, and hybrid).

As shown in *Figure 1*, there are several steps involved in the development and optimization of microcapsules and micro-particles for corrosion indicators and inhibitors. These include: selection of encapsulation media, selection of encapsulation method, selection of microcapsule wall materials, and microcapsule/micro-particle 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, 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 stability, of the microcapsules. 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 microcapsules have been previously reported.^{9, 24, 27, 28} This article highlights the developing and test results obtained with pH-sensitive micro-particles.

pH-SENSITIVE MICRO-PARTICLES

Results obtained during the development of pH-sensitive microcapsules as delivery systems for corrosion indicators and inhibitors²⁴ led to the conclusion that the delivery systems for all three corrosion management functions would be different depending on the indicator or inhibitor and the type of coating in which the carrier would be incorporated. While larger size self-healing microcapsules that contain liquid film-forming agents are needed for effective healing agent delivery to repair mechanical damage,²⁹ there is no benefit in having a large size for corrosion indicator or inhibitor delivering microcapsules. On the contrary, large microcapsules are more likely to break during coating mixing and application and more likely to cause coating defects. The desired size for a pigment-grade microcapsule is from sub-microns to a few microns. As a result, indicator and inhibitor microcapsules were optimized to obtain smaller sizes, better mechanical properties of the capsule walls, and a final product in free flowing powder form.²⁵⁻²⁷

During the microcapsule optimization process for the delivery of corrosion indicators and inhibitors, it was discovered during the proof-of-concept experiments for autonomous corrosion

indication that it would be desirable to increase the concentration of the corrosion indicator in the microcapsule core above the value allowed by the solubility. This led to the development of pH-sensitive micro-particles to allow the incorporation of solid corrosion indicators and solid corrosion inhibitor to eliminate the limitations imposed by the solubility of the active ingredient.⁹

While damage detection sensors and tools are being developed to aid corrosion inspection, a protective coating with an integrated corrosion-sensing function is highly desirable.

The newly developed micro-particle formulation has the following additional benefits: (1) low energy requirements for the encapsulation process: only a low mixing speed is required for very small size particle formation, compared with the high-shear energy needed for small microcapsule formulation; (2) elimination of the mechanical strength requirement for the delivery system: if the micro-particles are mechanically broken during paint mixing and application, this will only result in particles smaller than their original with no premature content release as with the microcapsule formulations; (3) easy processing and scalability to a final free-flowing powder product with pigment grade characteristics. These are important attributes for commercial applications.

MICRO-PARTICLE SYNTHESIS

A representative micro-particle synthesis process is shown in *Figure 2*. 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



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FIGURE 1—The development of the encapsulation process.

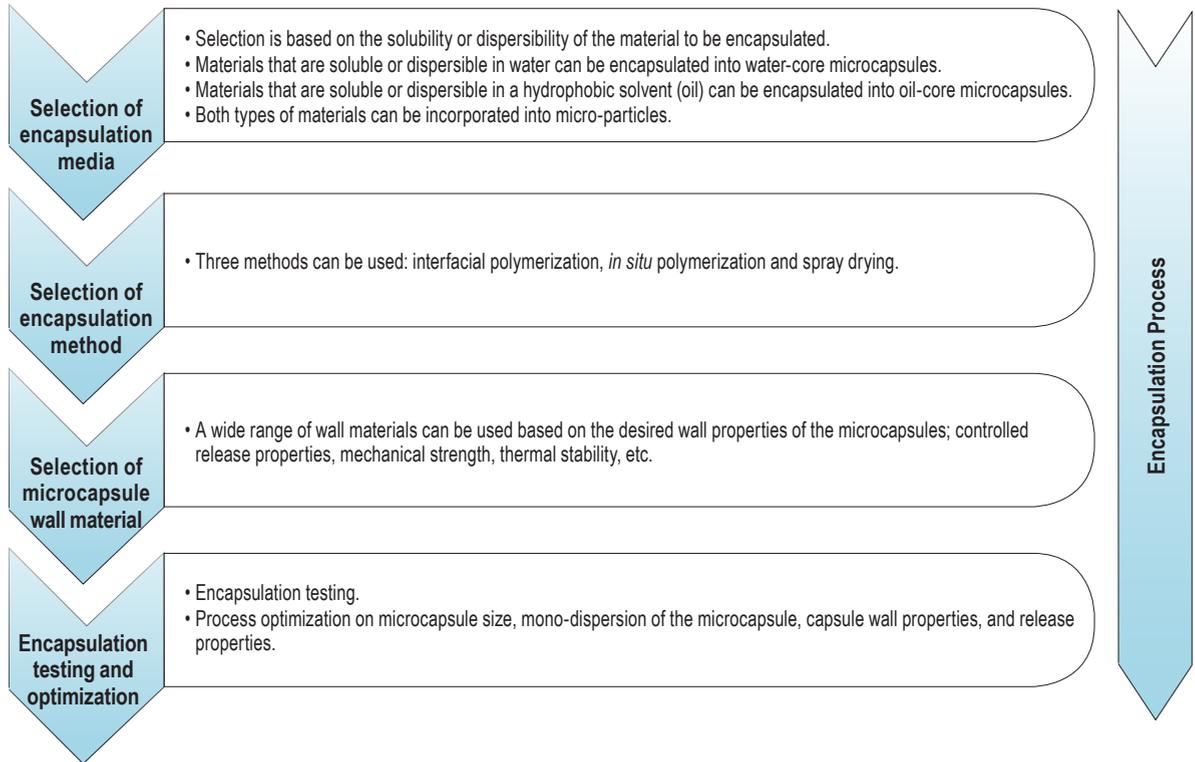
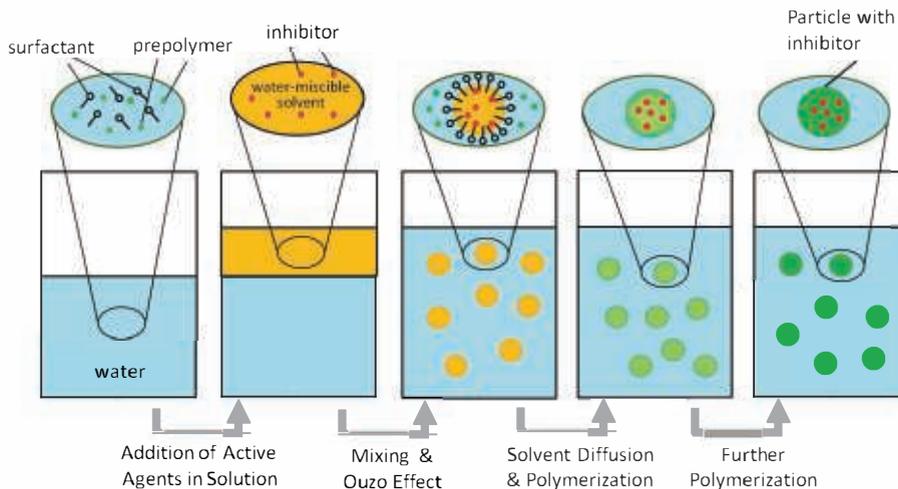


FIGURE 2—Micro-particle synthesis process.



with active ingredient. In the case of an inhibitor particle, the synthesis process includes first dissolving the inhibitor into a water miscible solvent, such as ethanol or isopropanol. The inhibitor solution is then added to a continuous water phase. This process allows the inhibitor to be incorporated into the particle rather than being dissolved into the water. While the process is not completely understood, it involves a somewhat spontaneous micro-emulsion process, similar to the Ouzo Effect, but less stable, by which the inhibitor solution is dispersed into droplets. The polymerization reaction then occurs at the interfaces of these droplets, which cause the inhibitor to be incorporated into particles before being dissolved into the water. Surfactants are used to control size and maintain particle distribution. A similar process is used to synthesize corrosion indicator micro-particles. A typical formula for pH-sensitive micro-particles with incorporated corrosion indicator is shown in Table 1. Scanning electron microscopy (SEM) images of pH indicator containing micro-particles are shown in Figure 3.

TABLE 1—Micro-Particle Formula with Incorporated Corrosion Indicator

REAGENT	MASS (g)
WATER	900
MELAMINE	45
FORMALDEHYDE (37%)	96
CROSSLINKER	32.5
SURFACTANT	6
INDICATOR	50
SOLVENT	133
CATALYST (ACID)	TO pH 5.5

Figure 4 shows the results from a salt immersion test of steel panels coated with a clear urethane coating blended with 10 wt% of phenolphthalein encapsulated into micro-particles. The panels were scribed and observed visually to detect the color changes associated with the onset of corrosion on the scribe versus exposure time.

FIGURE 3—SEM image of indicator micro-particles with color changing indicator phenolphthalein (left) and with fluorescent indicator fluorescein (right).

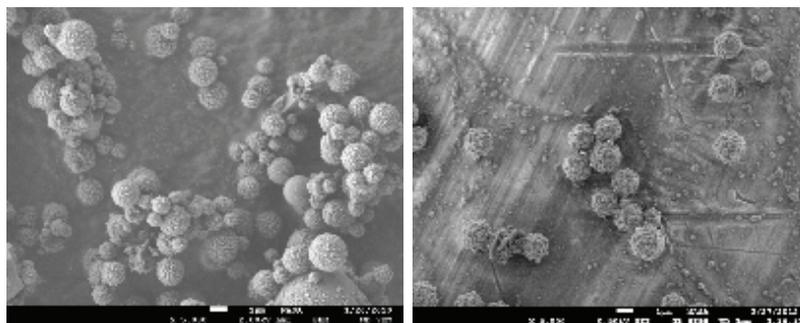
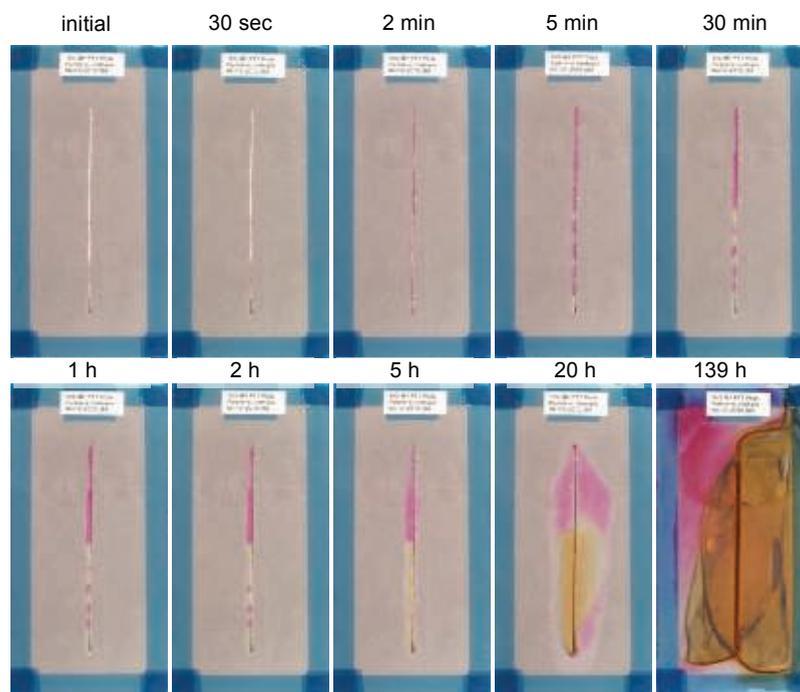


FIGURE 4—Corrosion indication test results.



CORROSION-SENSING COATING FORMULATIONS

Two corrosion-sensing coating formulations are reported in this section: one that contains phenolphthalein, a pH indicator which indicates corrosion with a visible color change, and a second that contains a corrosion indicator, which is a pH corrosion indicator through fluorescent changes, fluorescein.

Corrosion-Sensing Coating with Color Changing Indicator

An experimental corrosion-sensing coating was prepared by incorporating encapsulated phenolphthalein into a commercially available solvent-based 3k acrylic-urethane clearcoat coating. This coating was used to demonstrate the effectiveness of the indicator in early corrosion indication, as well as detection of hidden corrosion.



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Repeated observations confirmed that the onset of corrosion was visible in the scribe in less than 60 sec after immersion, which is considerably earlier than the two hours it takes for the typical color of rust to appear.

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 5* (left). Bolts tend to corrode on the hidden shaft area in advance of the visible corrosion detected 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 enhance the inspection process and increase the safety and reliability of the structure.

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 were prepared to find a coating system that would indicate crevice corrosion, as can be expected to occur in a nut and bolt assembly designed to duplicate the use of bolts to hold a structure. Some coating systems demonstrated the ability of the coating to indicate hidden corrosion as evidenced by the appearance of a purple color after 600 h of salt fog exposure (*Figure 5*, right).

Corrosion-Sensing Coating through Fluorescent Change

A commercially available solvent-based three-part acrylic-urethane clear coating was used for testing by incorporating fluorescein encapsulated into micro-particles into the coating at 0.05 wt%. The coating was then drawn down onto 3 in. x 2 in. R type Q-Panels®. After curing, the coated panels were taped to the bottom of polystyrene well plates and scribed at the center of the panel. A baseline reading was taken for all panels using the TECAN M1000® infinite fluorescence spectrometer before exposure to salt solution. After

TABLE 2—Fluorescence Spectroscopy Instrument Parameters

DEVICE	TECAN INFINITE M1000 PRO
PLATE	1536 FLAT BOTTOM TRANSPARENT POLYSTYRENE WELL PLATE
MODE	FLUORESCENCE TOP READING
EXCITATION WAVELENGTH	494 NM
EMISSION WAVELENGTH	525 NM
EXCITATION BANDWIDTH	5 NM
EMISSION BANDWIDTH	5 NM
GAIN	100 MANUAL
FLASH FREQUENCY	400 HZ
INTEGRATION TIME	20 μs
LAG TIME	0 μs
SETTLE TIME	100 MS
Z-POSITION (MANUAL)	20000 μm

the initial reading was taken, approximately 50 mL of 5% aqueous sodium chloride (NaCl) solution was added to the well plates (sufficient to cover the entire panel) and the plates were sealed and placed back into the spectrometer. The parameters used for the fluorescence spectrometer are provided in *Table 2*.

FIGURE 5—Conceptual illustration of hidden corrosion indication in structural bolts (left). Indication of hidden corrosion after 600 h of salt fog exposure (right).



All samples were scanned every 15 min. After the measurements were completed, the panels were removed and rinsed with deionized (DI) water and photographed. The resulting panels were further examined using a Keyence VHX-600® digital microscope at 100X magnification to correlate areas of high fluorescence intensity with corrosion spots on the panels observed visually and via fluorescence spectroscopy.

A Zeiss LSM 710® confocal fluorescent microscope was also used to observe the test panels before and after salt immersion exposure. *Figures 6–8* show these images. The images show the fluorescein particle distribution in the coating before the salt water exposure, and the fluorescence intensity next to the corrosion sites (near the scribe area). While the 2D image confirms the local fluorescent indication signal, the 3D images reveals the intense fluorescent emission from the coating/metal interface where local pH changes directly correlate with metal hydroxide formation, which is indicative of the onset of the corrosion process.

Figure 9 summarizes the TECAN reflectance fluorescence spectroscopy scanning composite image on the coated cold rolled steel panel during salt immersion exposure up to 5.5 h, with an artificial defect in the middle. Although the main event is at the defect sites, there are many other corrosion events occurring as early as one hour.

Figure 10 shows that after 15 h salt water immersion testing, the only visible corrosion to the unaided eye is at the induced defect point at the middle of the panel (picture on the left), while the fluorescence scanning images show many more early corrosion activity sites (middle). Optical microscope images at 100X magnification reveal very small corrosion spots corresponding to some of the corrosion events detected by the TECAN scanning method (optical microscopy images at right).

FIGURE 6—Confocal scanning laser microscopy 2D images (488 nm) of fluorescent corrosion sensing coating applied to cold rolled steel. Unexposed panel (left); near scribe after 15 h immersion in 5% NaCl (right).

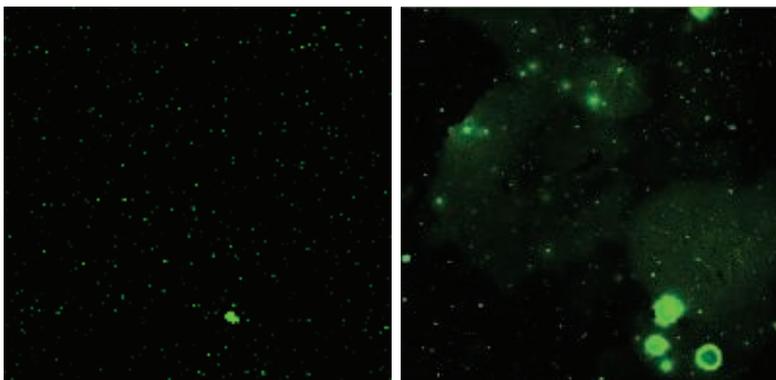


FIGURE 7—Confocal scanning laser microscopy 3D images (488 nm) of fluorescent corrosion sensing coating applied to cold rolled steel. Unexposed panel (left); near scribe after 15 h immersion in 5% NaCl (right).

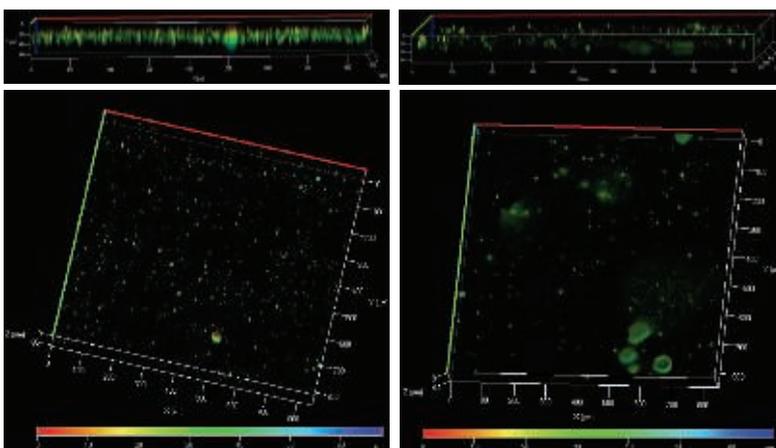
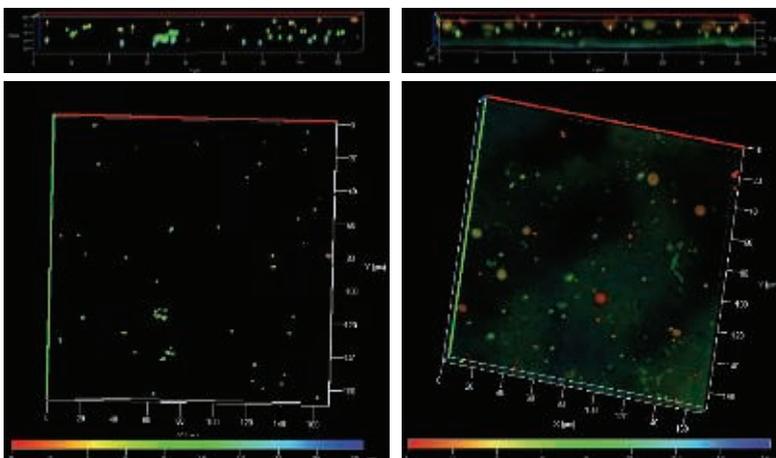


FIGURE 8—Confocal scanning laser microscopy 3D images (488 nm) of fluorescent corrosion sensing coating applied to cold rolled steel. Unexposed panel (left); near scribe after 15 h immersion in 5% NaCl (right) (zoomed in).





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SUMMARY

Microencapsulation has been developed and optimized to incorporate desired corrosion control functionalities, such as early corrosion detection and inhibition, through corrosion-initiated release of corrosion indicators and inhibitors, as well as self-healing agent release triggered by mechanical damage. The initial efforts involved the development of pH-sensitive microcapsules for the delivery of corrosion indicators. Results from the corrosion indication function tests indicated that it would be desirable to achieve a higher concentration of the encapsulated active ingredient, above what can be obtained based on the limitations imposed by its solubility.

This finding led to the development of pH-sensitive micro-particles (organic, inorganic, and hybrid). This article presents highlights of the development and results obtained with the organic micro-particles. Inorganic as well as hybrid (organic/inorganic) micro-particles are currently under development to increase the versatility of the corrosion-triggered delivering systems for corrosion management. ❄

FIGURE 9—TECAN scan images show local corrosion events.

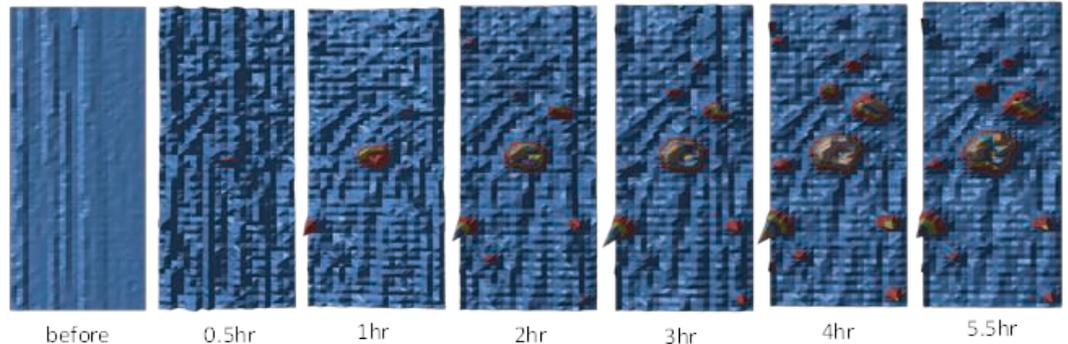
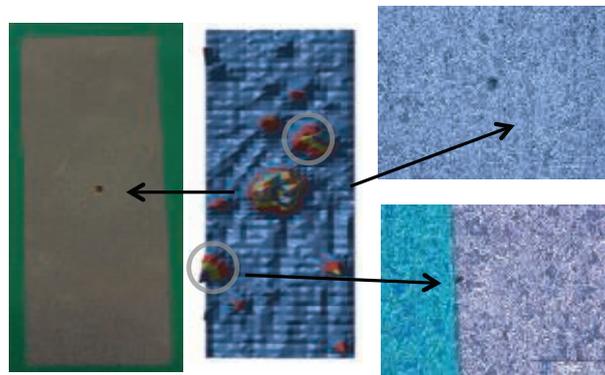


FIGURE 10—Fluorescent corrosion sensing coating for early corrosion detection. TECAN scan image after 5.5 h salt water immersion testing is in the middle, while a picture and optical microscopy images (100X) of the panel after 15 h of salt water immersion testing are on the left and right.



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