LIFE EXTENSION IN PROTECTIVE COATINGS VIA SELF-HEALING TECHNOLOGY

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ABSTRACT

As the field of self-healing materials continues to grow, novel self-healing concepts and chemistries are being developed for a variety of applications including coatings. Self-healing functionality is typically considered for incorporation in coatings to solve two basic challenges including restoration of aesthetic properties and restoration of protective function. In this talk I will compare these challenges and discuss the capability of existing technologies to meet them. I will then discuss examples of the development and application of self-healing chemistries to protective coatings and the level of success achieved in autonomic repair of coatings that have been damaged via a variety of mechanisms. These examples will include a range of laboratory and commercial formulations evaluated with a target of real world deployment in the near future.

1. INTRODUCTION

Introduction to the Concept of Self-Healing Materials

Self-Healing materials are a class of smart materials that are capable of repairing themselves, when they are damaged, at ambient temperature, without any external intervention. Self-healing in materials is a bio-mimetic concept modeled after the capability of biological systems to autonomically repair or re-generate after damage. Given the definition of self-healing technology provided above and the biological systems that these technologies are modeled after, not all technologies commonly referred to as self-healing are truly self-healing. Healing technologies can broadly be classified as autonomic and non-autonomic healing technologies. These classifications and representative examples are described below.

Non-Autonomic Healing in Materials

There are many examples of technologies that impart the ability to respond to specific external stimuli such as heat or UV radiation for healing. These technologies hearken back to the original examples of crack healing in polymers, which utilized solvents and heat to repair cracks.[3] More recent examples of heat-initiated healing technologies include re-mendable polymers, which have demonstrated crack healing based on Diels–Alder and retro-Diels–Alder reactions at temperatures between 90 ºC and 120 ºC.[1,2] Other examples of heat-initiated healing technologies include polyurethane resins capable of crack healing when heated above their class transition temperatures.[2] Oxetane-substituted chitosan polyurethane networks capable of crack healing when exposed to UV light have also been reported.[2]

Another recently reported UV light-initiated healing technology is based on supramolecular materials formed by metal–ligand interactions.[4] Upon exposure to UV light, the metal-ligand functionalities in the material are disengaged facilitating flow of the material to minimize or repair defects. In addition to the external intervention required, the incorporation of molecular functionality included to facilitate the healing response will likely result in an intrinsically less robust material. As such, the majority of these systems are better suited to aesthetic applications in which the damage can be easily observed and addressed, and for which durability is not of the highest priority.

Autonomic Healing in Materials

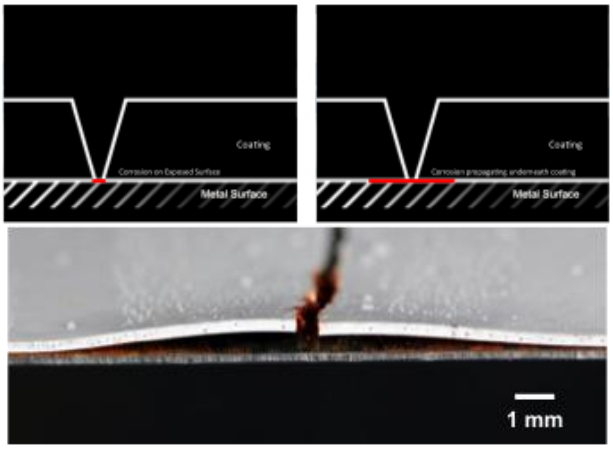
Technologies that fall under this classification are designed such self-healing occurs at the ambient temperature of the system in its specific application. The most successful approaches to designing systems capable of autonomic healing have been based on the compartmentalization of a healing agent such that damage triggers its release into the site of damage. Once in the site of damage, the healing agent then solidifies through a curing mechanism restoring at least part of the materials' original mechanical properties. Some examples of self-healing concepts capable of autonomic healing include those in which the healing agent is compartmentalized in microcapsules, hollow fibers and microvascular networks.[1,2] Since microcapsules can be easily incorporated into existing commercial polymeric materials, microcapsule-based technologies appear to currently be the most feasible pathway to commercial self-healing applications.

Self-Healing for Corrosion-Resistance and Life Extension in Protective Coatings

A 2002 study by the National Association of Corrosion Engineers (NACE) estimated the direct cost of corrosion to the U.S. economy in 1999 at about 3% of GDP ($ 276 billion). At the same proportion of GDP, these numbers are estimated to be closer to $870 billion today and about $ 2 trillion globally. This challenge has traditionally been met by developing improved coatings via the use of better formulation ingredients (resin, dispersants, corrosion inhibitor etc.) as well as improved formulation techniques. While these efforts often lead to practically improved coatings, they do not address the fact that when the coating is physically damaged, the underlying substrate is exposed to the environment. Once exposed, the substrate rusts and the propagation of rust away from the initial damaged region leads to a loss of adhesion of the coating to the substrate. The loss of adhesion renders the coating incapable of performing its protective function leading to a need for repair or replacement (Figure 1).

Historically, the concept of self-healing was employed in the coating's industry by the use of hexavalent chromium in various coating applications.[5] When a chromated product is exposed to the atmosphere due to damage of the coating, hexavalent chromium slowly leaches out of the film into the damaged region where it is reduced to form a new trivalent chromium oxide layer that restores passivation to the damaged area. Hexavalent chromium compounds are known to be toxic and carcinogenic and are being phased out of most applications. Replacements for this

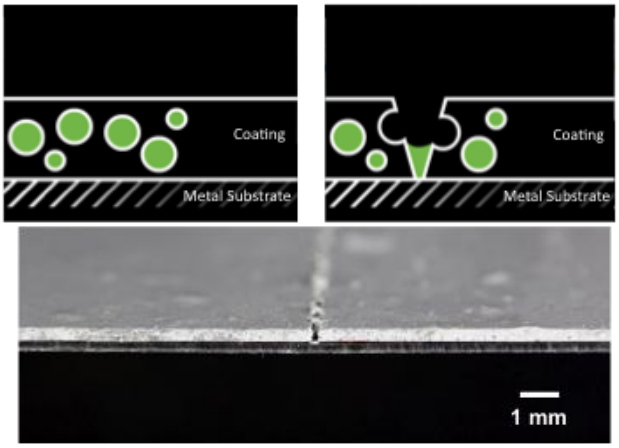
technology to date however have not been as effective as they have lacked the self-healing functionality of hexavalent chromium.



(a) (b) (c)

Figure 1: **Traditional Coating.** Schematic demonstrating the effect of damage to a traditional coating. **(a)** The area exposed to the atmosphere is no longer protected and begins to rust. **(b)** Over time the rust propagates underneath the coating, a process known as undercutting. **(c)** Undercutting of a polyurethane mastic coating on the surface of a cold-rolled steel substrate (coating thickness approximately 5 mils).

White and co-workers at the University of Illinois were the first to report the development of a self-healing polymeric material [6]. The original system was based on a common epoxy resin incorporating microcapsules containing dicyclopentadiene (DCPD) and particles of Grubbs' catalyst. Damage in the form of a crack propagating through this material ruptured the microcapsules causing DCPD to be released into the crack plane where upon contact with the catalyst particles a polymerization reaction was initiated [6]. Building on this initial concept for self-healing polymeric materials, several new chemistries have been developed for application in novel self-healing materials for various applications including self-healing coatings [7,8], composites [9] and elastomers [10]. In addition to expanding the scope of potential applications for self-healing materials, these new chemistries utilized more economical raw materials essential for commercialization.



(a) (b) (c)

Figure 2: **Traditional Coating with Self-Healing Additive.** Schematic demonstrating the effect of damage to a self-healing coating. **(a)** Microcapsules containing healing agent are mixed in to the coating prior to application on the substrate. **(b)** Damage to the coating ruptures the microcapsules releasing healing agent into the site of damage. **(c)** Polymerized healing agent restores protective function to a polyurethane mastic coating on the surface of a cold-rolled steel substrate, eliminating undercutting (coating thickness approximately 5 mils).

This talk will focus on using similar chemistries for application in the development of self-healing protective coatings. When such coatings are damaged, the microcapsules release a customized healing agent formulation to the site of damage (Figure 2b). Once in the site of damage, the healing agent polymerizes and restores the protective function of the coating thereby preventing undercutting that would have been prevalent in the absence of self-healing functionality (Figure 2c).

Damage Mechanisms and Healing Response

During the talk, I will refer to three categories of damage based on the size of the damage and the amount of healing agent available for delivery. These categories, referred to as internal damage, visible damage and large-scale damage are described in more detail below:

Internal damage: This is damage that occurs deep within the coating film and is usually invisible from the surface. This kind of damage takes the form of multiple micro-cracks that propagate over time to form a network through which the substrate is exposed to the environment. Damage in the form of micro-cracks typically originates from failure at the molecular level due to cycling between temperature extremes, UV-radiation, adverse chemical conditions or repeated impact to the coating. We have successfully demonstrated self-healing systems that facilitate the complete repair of this scale of damage. Cold-rolled steel panels coated with a polyurethane coating containing one of our products and subjected to impact via a gravelometer or an impact tester followed by exposure to an accelerated corrosion test exhibited no rust on the surface of the coating. Since the micro-cracks formed in these coatings as a result of the impact are typically less than 10 μm, there was enough healing agent available to completely heal the cracks. Similarly coated panels excluding the self-healing additive were observed to rust in accelerated

corrosion testing, as the micro-cracks formed in these coatings were incapable of self-healing (Figure 3a).

Visible Damage: This kind of damage typically takes the form of a 50 μm scribe that is often introduced to a coating to evaluate its protective capabilities by measuring creep from scribe after exposure to an accelerated corrosion test. Our observations have been that if the additive microcapsules are at least on the same order of magnitude in size or greater than the width of the scribe, there will be enough healing agent delivered to generate a new barrier at the bottom of the scribe. The new barrier formed protects the substrate from the environment thus preventing rusting that would have otherwise taken place in the absence of the self-healing additive (Figure 3b).

Large-Scale Damage: This is damage that is considered larger than the two forms of damage already discussed. If we consider damage of this scale in the form of a scribe (e.g. $\geq$ 500 μm), there will not be enough healing agent to form a barrier that completely covers the bottom of the scribe. In the event of such damage, microcapsules at the edges of the damaged region will be ruptured and the healing agent released will flow to the bottom of the scribe where once polymerized it will seal the edge of the damage. As such, although some part of the scribe will remain exposed and will therefore eventually rust, the rust will be contained to a much smaller area and the self-healing functionality will prevent undercutting and loss of adhesion (Figure 3c).

Once delivered, the healing agent provides protection to the site of damage via a three-step process. The first step is moisture-repulsion. All of our healing agent formulations are designed to be hydrophobic and upon release into the site of damage immediately begin repelling moisture from the substrate thereby providing instantaneous temporary protection. In the next step, as solvents in the formulation begin to evaporate, the polymeric binders mix, coalesce and polymerize to form a gel which hardens over time to form a robust binder capable of providing longer term protection. In the final step, custom additives present in the formulation elevate the formulation from performing simply as binder to performing more like a fully formulated coating with the typical associated benefits.

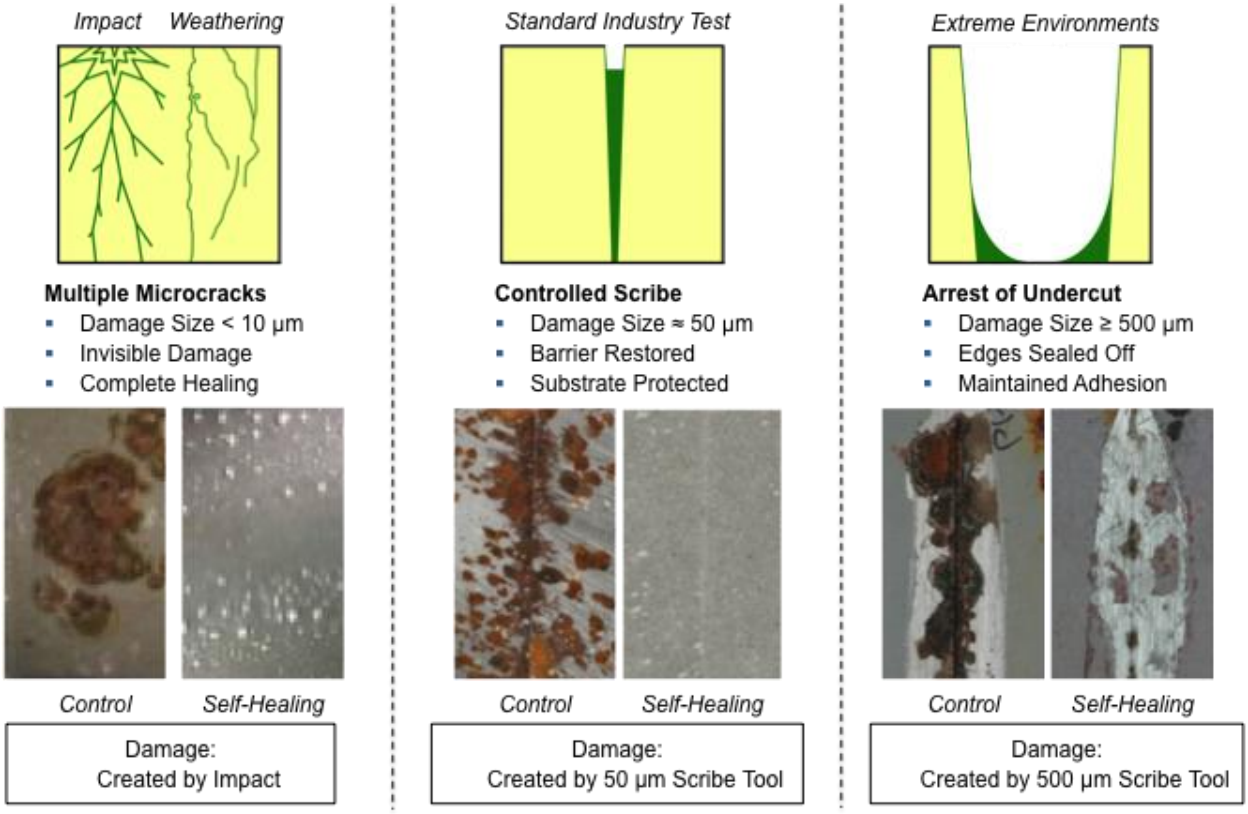


Figure 3: Scales of coating damage and the corresponding self-healing mechanisms. **(a)** Internal damage. **(b)** Visible damage. **(c)** Large-scale damage.

2. MATERIALS AND METHODS

Dual Capsule Systems Based on Vinyl-Terminated PDMS

The two varieties of microcapsules in this dual capsule system are added to the coating formulation at a 1:1 ratio. Damage to the coating resulting in mechanical failure will rupture both sets of microcapsules releasing their contents to the site of damage where they will mix, polymerize and restore the coating's protective function (Figure 4). For the purpose of this paper, this system is referred to as Series 1. Series 1 has demonstrated good performance in a range of coatings including flexible and compliant coatings such as polyurethane and silicone coatings, various powder coatings, epoxies, water and solvent-based direct-to-metal coatings. Demonstrating excellent thermal stability, the self-healing functionality of Series 1 was observed in powder coatings that were cured at temperatures as high as 400 °F.

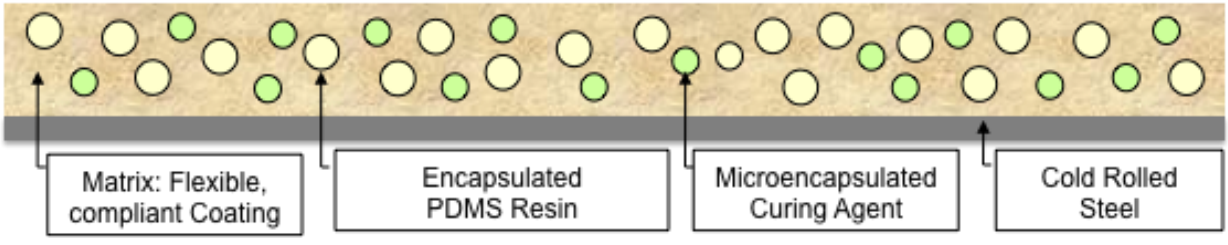


Figure 4: Dual-capsule system based on vinyl-terminated PDMS.

One-Capsule Systems Based on Epoxy Chemistry

The single-capsule concept on which this self-healing system is based is referred to as a solvent-induced healing chemistry and was first demonstrated in polymerized epoxy resins in which it was shown to facilitate greater than a 100% recovery of the original fracture toughness of the material. [11] For the purpose of this paper this system will be referred to this system as Series 2. The resulting microcapsules are formulated into an epoxy coating such that damage to the coating ruptures the microcapsules releasing the healing agent into the site of damage. Once in the site of damage, the solvent elutes out residual curing agent functionality from the polymerized coating matrix, and promotes a reaction with the epoxy resin also delivered to the site of damage. A schematic summarizing the Series 2 self-healing system is shown in Figure 5.

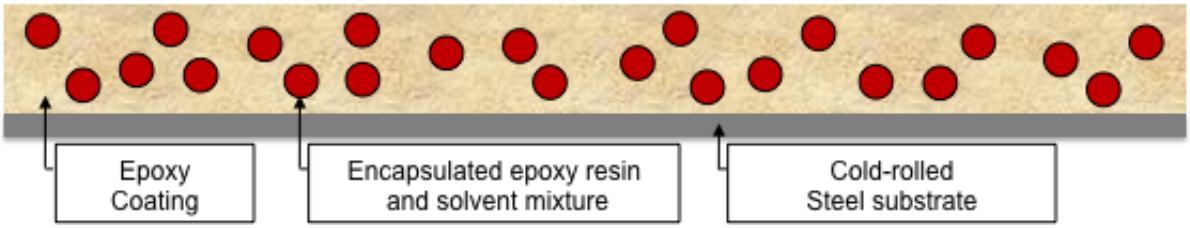


Figure 5: Dual-capsule system based on solvent-induced epoxy healing chemistry.

Microcapsule Preparation

Self-healing systems discussed in this paper are based on microcapsules prepared using previously reported shell walls and procedures. [7,12,13]

Preparation of Coating Formulation and Application

For all results to be discussed, microcapsule-based products were post-added into the coating and mixed in with the help of mechanical stirring maximum stirring rates of 2000 RPM. The resulting formulation was then drawn down on the target substrate using a drawdown bar. The coating was then allowed to cure for the recommended cure time at room temperature (typically 1 to 7 days) after which it was scribed using scribe tools of varying widths. Unless otherwise specified, the samples were then allowed to heal at RT for 24 h prior to accelerated testing (ASTM B117). After exposure to the accelerated test, the samples were then evaluated for corrosion creep or loss of adhesion. For cases in which adhesion loss or corrosion creep fron scribe is reported, the measurements were made by measuring from the center of the scribe to edge of the corrosion creep or area of adhesion loss. A total of six equi-distant measurements were taken for each scribe and the average recorded.

3. RESULTS AND DISCUSSION

Representative Results from a Dual-Capsule System

An example of the use of Series 1 in an un-pigmented epoxy coating applied on cold-rolled steel (CRS) panels is shown below (Figure 6). The CRS panels were lightly abraded followed by cleaning by wiping with acetone. Un-pigmented systems were

used in the experiments discussed in this paper to observe performance due to restoration of barrier properties alone, excluding the effect of pigments that are typically present in the standard formulation. After exposure to ASTM B117 conditions for 1000 h, the samples were evaluated and the resulys are summarized in Figure 6. Loss of adhesion around the scribes was evaluated by using ASTM-specified adhesive tape applied along the scribe and rapidly ripped off after about 1 min. This action typically causes areas with adhesion loss to raise up from the steel panel. The area of adhesion loss was outlined immediately and is labeled in Figure 6. While the control sample exhibited significant loss of adhesion, the self-healing sample containing Series 1 at 5 wt% exhibited practically no loss of adhesion for the 186 micron scribe and less than 2 mm of adhesion loss for the 500 micron scribe.

Representative Results from a One-Capsule System

Similar results were oberved for Series 2 in a different industrial epoxy coating also applied on CRS panels prepared and cleaned as described above. While the control sample exhibited significant loss of adhesion and corrosion creep from scribe, the corresponding self-healing sample containing 5 wt% Series 2 exhibited no loss of adhesion and minimal corrosion creep for both 186 micron and 500 micron scribes after 1024 h exposure to ASTM B117 conditions. These results represent unprecedented corrosion resistance for coating formulations that do not include any pigment.

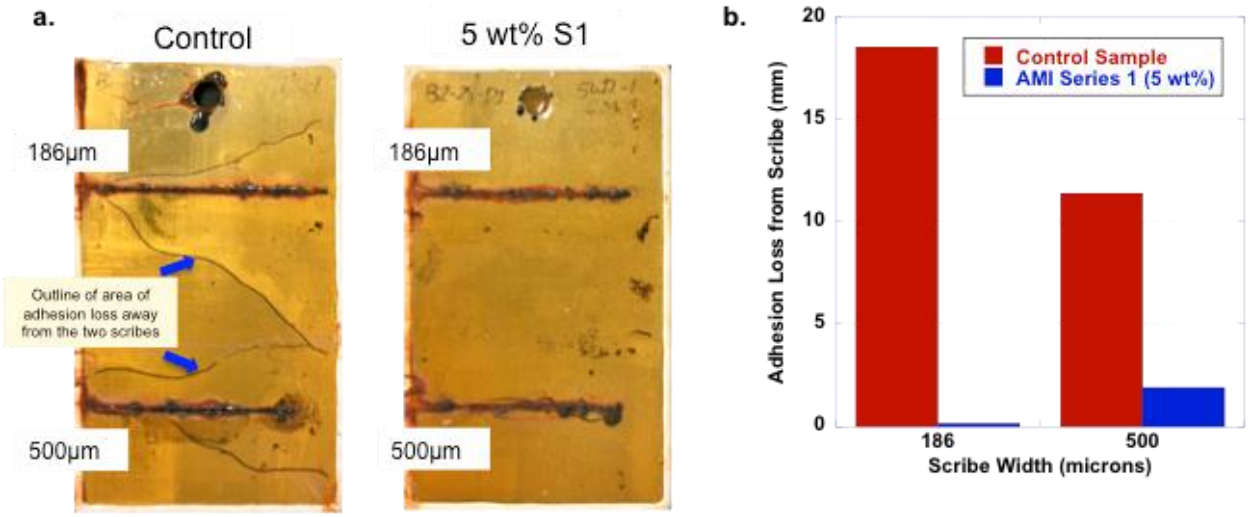


Figure 6: Self-healing performance of Series 1 in an epoxy marine coating.

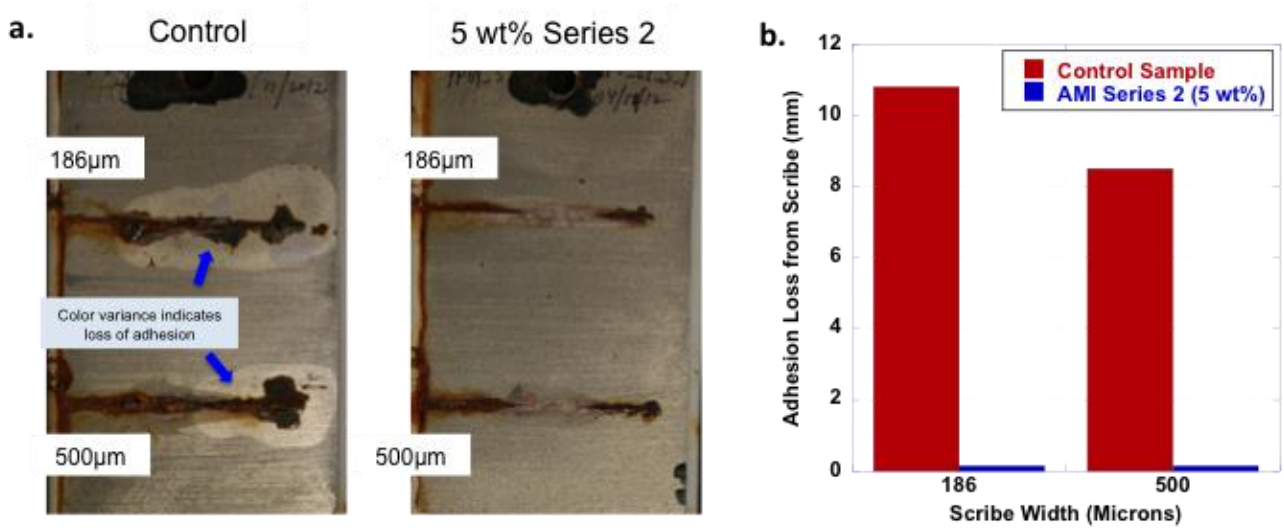


Figure 7: Self-healing performance of Series 2 in an industrial epoxy coating.

4. CONCLUSIONS

In addition to the background provided on the emerging field of self-healing coatings, the results of the self-healing performance due to two different self-healing additives in un-pigmented coatings were discussed. Similar observations have been made in fully pigmented formulations as well. Self-healing additives based on microencapsulation have been demonstrated to improve the corrosion resistance and adhesion of protective coatings damaged via a wide variety of mechanisms. While various pigments and corrosion inhibitors typically used in coating formulations might effectively resist corrosion prior to damage, microcapsule-based self-healing systems present a complementary technology for overall improved corrosion resistance.

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