2019 Award Nomination

Title of Innovation:

Self-Healing Additives for Corrosion Resistance

Nominee(s)

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All Nominees are from Autonomic Materials, Inc.

Category:

(select one below)

Coatings and Linings	Instrumentation
Cathodic Protection	Testing
Materials Design	Integrity Assessment
Chemical Treatment	Other—fill in

Dates of Innovation Development:

January 2014 to January 2018

Web site:

www.autonomicmaterials.com

https://coatings.specialchem.com/centers/self-healing-coatings

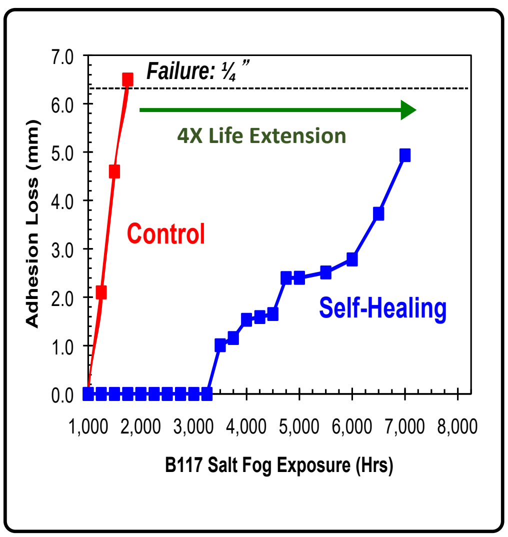
Summary Description:

In a 2016 report by the National Association of Corrosion Engineers (NACE), the global cost of corrosion was estimated to be about US$ 2.5 trillion, which amounts to about 3.4% of global Gross Domestic Product (GDP). Industries such as oil and gas, infrastructure maintenance and marine that maintain a disproportionate amount of their assets in extremely corrosive environments bear a disproportionate amount of these costs. Add to these costs the environmental and individual safety consequences of material failure due to corrosion and the case for investing in new technologies geared towards improving corrosion protection can hardly be overstated.

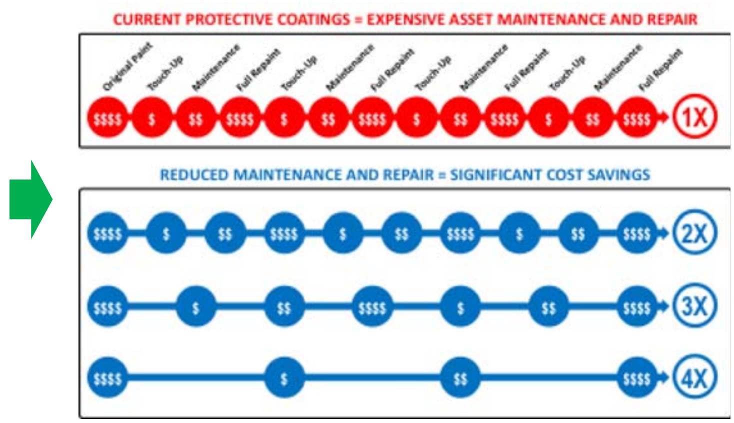
Well-designed protective coatings perform admirably in the protection of metal substrates that may be subject to corrosive environments. Once damaged in a way that exposes the underlying substrate, however, corrosion of the substrate will begin and typically propagates in the form of undercutting at the coating-substrate interface. Undercutting compromises the coating's adhesion to the substrate leading to delamination and impairment of the coating's ability to protect the substrate.

The innovation disclosed herein is in the form of an additive comprised of a microencapsulated healing agent containing an epoxy resin, a polar diluent, corrosion inhibitors and adhesion promoters. The microcapsules can be formulated into water-borne and solvent-borne liquid epoxy coatings, zinc-rich primers, powder coatings and fusion-bonded epoxy coatings. Once fully cured, damage to these coatings ruptures the microcapsules releasing the healing agent into the site of damage where it polymerizes, seals the edge of the damage, delays undercutting and facilitates maintenance of the coating's adhesion. The improved maintenance of adhesion keeps the coating in service longer thereby minimizing the extent of recoating and maintenance required and lost productivity due to downtime over the lifetime of the asset. A schematic illustrating the cost savings associated with the lifetime extension of a coating used in a corrosive environment is provided below:

4X LIFE EXTENSION DEMONSTRATED IN COMMERCIAL SELF-HEALING COATING*



IMPROVED COATING LIFETIMES LEAD TO A DECREASE IN THE NUMBER OF PAINTING ACTVITIES AND TOTAL LABOR EXPENSE



*Accelerated Exposure

Full Description:

(Please provide complete answers to the questions below. Graphs, charts, and photos can be inserted to support the answers.)

1. What is the innovation?

The innovation described here is an additive comprised of a liquid healing agent core formulation encapsulated by a polymeric shell, which upon incorporation into a coating formulation imparts self-healing functionality to the coating. The liquid core formulation consists of an epoxy resin, a polar diluent, a corrosion inhibitor and an adhesion promoter. The resulting microcapsules are incorporated into an epoxy coating formulation prior to application to a metal substrate. Damage to the coating ruptures the capsules releasing the healing agent into the site of damage. Once in the site of damage, the polar diluent penetrates the network structure of the epoxy thermosetting coating carrying the epoxy resin to a site of available cross-linking functionality within the matrix. The resulting initiation of cross-linking facilitates curing of the epoxy resin present in the healing agent formulation released at the site of damage restoring the barrier property of the coating and sealing the edge of the damage. For common epoxy-based coating systems, available cross-linking functionality takes the form of a stoichiometric excess of primary amines and amides due to the formulation of the coating or partially unreacted amine or amide functionality available due to the fact that most epoxy-based formulations are cured below their glass transition temperatures. The product resulting from this innovative technology has been branded as AMPARMOR™ 2000 Series and is referred to as such in future sections.

2. How does the innovation work?

The best coating systems designed for the protection of metal assets typically perform remarkably well until they are compromised in some way. The lifetime of a coating system is therefore defined by its ability to adequately provide protection to the underlying substrate in service. Once compromised, the coating will rapidly degrade, leading to the exposure and oxidation of the underlying substrate (Figure 1a). In the presence of self-healing additives such as described above, to the extent failure in the coating stems from a mechanical breach of the coating's protection of the underlying substrate, healing agents released to the site of damage when damage occurs restore the protective properties of the coating thereby extending the protection of the substrate in service, and in effect delaying the eventual oxidation of the underlying substrate (Figure 1b).

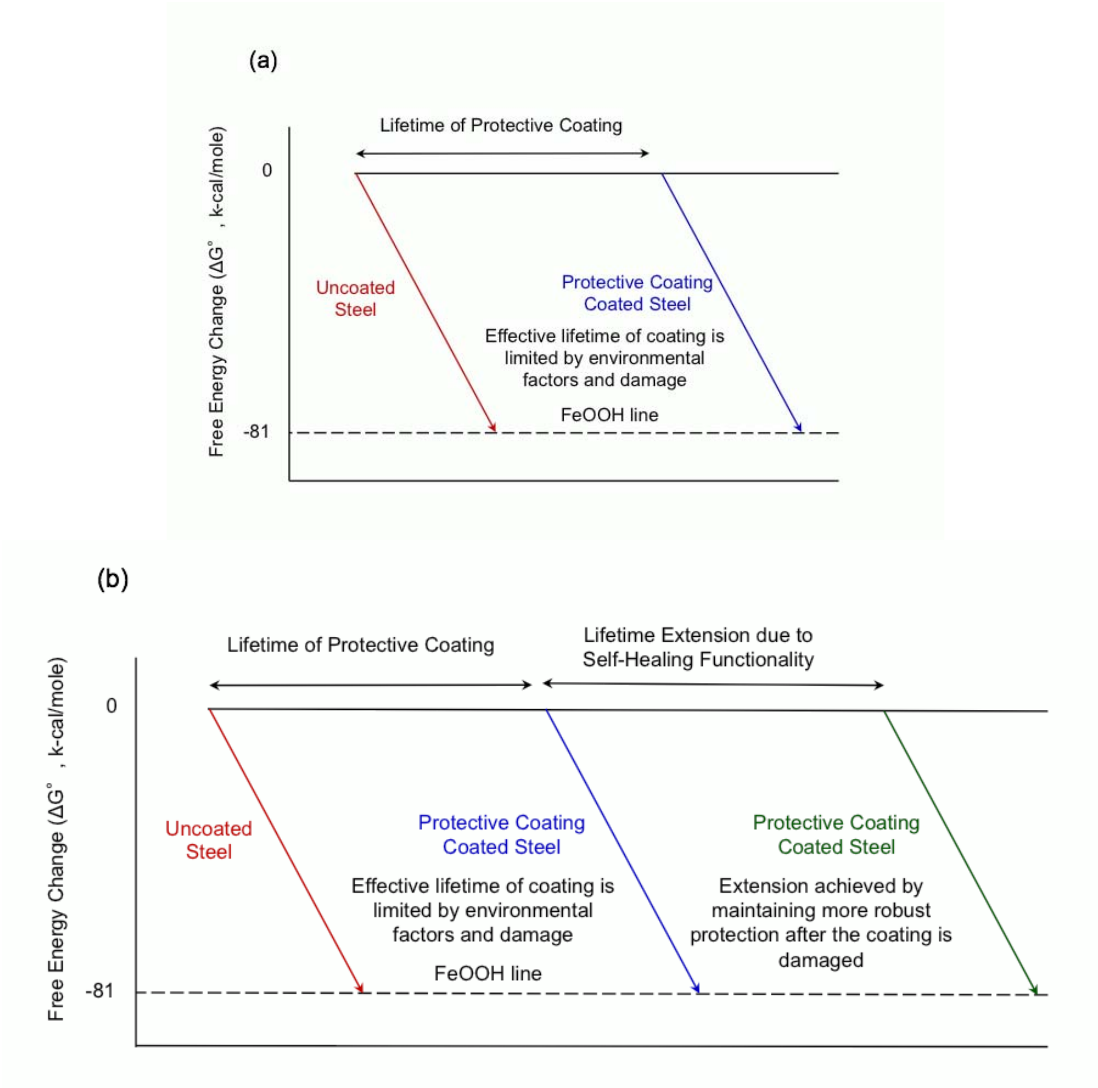
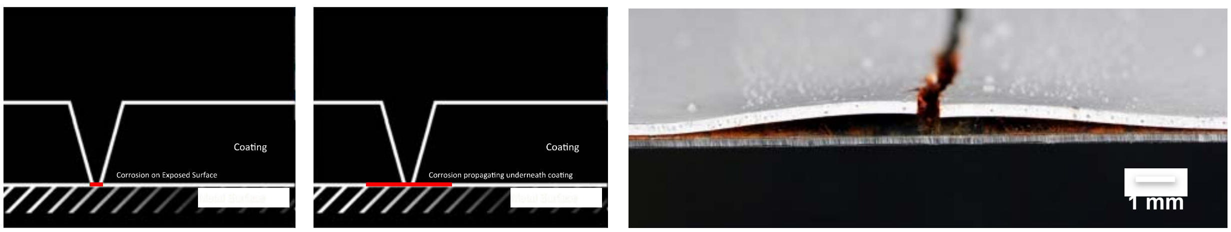


Figure 1. *(a) The role of a protective coating in extending the lifetime of the underlying substrate. The free energy change of the oxidation of metallic iron to form ferric oxyhydroxide is illustrative of the corrosion of a metallic substrate in the presence and absence of a protective coating (P. A. Schweitzer, Paint and Coatings, Applications and Corrosion Resistance, CRC Press, Taylor & Francis Group, 2006). (b) Extension of the protection of the underlying substrate due to self-healing functionality.*

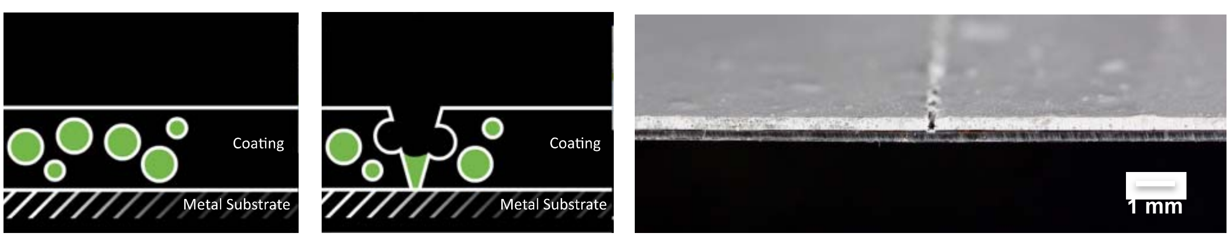
3. Describe the corrosion problem or technological gap that sparked the development of the innovation? How does the innovation improve upon existing methods/technologies to address this corrosion problem or provide a new solution to bridge the technology gap?

The challenge posed by the entropic inevitability of corrosion has been met over the years by efforts to improve the alloys that comprise metal substrates with the aim of retarding their oxidation and the development of coatings with improved properties via the use of better formulation ingredients (resin, dispersants, corrosion inhibitor etc.) as well as improved formulation techniques. While these efforts have led to improved performance, they do not address the fact that when the coating is mechanically damaged, the underlying substrate is exposed to the environment. Once exposed, the substrate corrodes rapidly and the propagation of corrosion 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 of the coating (Figure 2). The failure (or inability) to account for the increased assault at the coating-substrate interface in a damaged coating is a missed opportunity in the design of coatings that can be addressed by incorporating self-healing functionality that will help the coating maintain its adhesion for longer exposure times after damage. Mechanical damage such as scratches and micro-cracks that stem from impact from typical use and weathering conditions are common in most protective coating applications. These damage mechanisms to a coating containing self-healing additives will result in the rupture of the microcapsules followed by release of the healing agents into the site of damage where polymerization occurs, sealing off the damage and preventing adhesion loss due to moisture penetration or undercutting at the coating-substrate interface (Figure 3).



(a) (b) (c)

Figure 2. *Traditional coating. Schematic demonstrating the effect of damage to a traditional coating. (a) The area exposed to the environment is no longer protected and begins to corrode. (b) Over time the corrosion propagates underneath the coating, a process known as undercutting. (c) Undercutting of a polyurethane mastic coating on the surface of a cold-rolled steel (CRS) substrate (coating thickness approximately 125 microns).*



(a) (b) (c)

Figure 3. *Traditional coating incorporating 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 self-healing polyurethane mastic coating on the surface of a CRS substrate, eliminating undercutting (coating thickness approximately 125 microns).*

The additive is manufactured via a microencapsulation process from an oil-in-water emulsion. The oil phase is comprised of the healing agent blend. The polymeric shell wall which contains the healing agent in the product is built via an in-situ polymerization process. A slurry results from the encapsulation process, which can be used without further processing in water-borne coating applications or spray-dried for solvent-borne or powder coatings. For all coating formulations, the capsules will occupy volume in the coating formulation and will contribute to the pigment volume concentration (PVC) of the coating. As such formulation adjustments must be made to ensure other properties of the coating that typically stem from the PVC are not compromised. The capsules can be added during the let-down stage of the coating batch-making process where viscosities are typically lower and germane shear rates are also typically lower. The capsules prepared for these applications range in sizes from 5 microns to 25 microns allowing for sizes similar to commonly used pigments and fillers and compatibility with coating dry film thickness of 25 microns and greater. Other than routine and expected adjustments to the formulation and following guidelines regarding order of entry, the incorporation of these additives into existing coating formulations does not require any meaningful changes to batch making or coating application processes thereby lowering the barriers to adoption of the self-healing technology.

4. Has the innovation been tested in the laboratory or in the field? If so, please describe any tests or field demonstrations and the results that support the capability and feasibility of the innovation.

A description of the results of evaluations performed in common coating systems used in the protection of metal substrates is provided below:

Powder Coatings

AMPARMOR™ 2000 has been evaluated in a variety of standard epoxy powder coatings, typically as part of a system incorporating a polyester topcoat. In these evaluations, AMPARMOR™ 2000 was blended with the epoxy powder coating via co-fluidization in an air-filled container. The resulting modified powder coating was then applied to either standard CRS panels or Bonderite® 1000 (B1000) pretreated CRS panels via an electrostatic spray gun and cured at 400ºF (204ºC) for 10 minutes, followed by application of a standard polyester top coat and curing for an additional 10 minutes. The epoxy primer layer and the polyester topcoat were both applied to a DFT of 4 mils (100 microns) each for a total DFT of 8 mils (200 microns). The coated samples were then scribed using a 500-micron scribe tool and allowed to equilibrate at room temperature for 24 h, after which the samples were exposed to ASTM B117 conditions. The samples were then removed from the salt fog at 250 h intervals, scraped perpendicular to the scribe to remove any dis-bonded coating prior to returning the panels to the salt fog. We refer to this approach to ongoing exposure and testing as a dynamic exposure/evaluation testing protocol. A summary of the results obtained for these systems is provided in Figure 4. With a creep from scribe failure specification of 0.25 inches in mind, the coated B1000 pretreated CRS panels were tested beyond 3500 h of salt fog exposure. While the control samples exhibited adhesion loss from scribe of greater than 0.25 inches (6.35 mm) prior to 2500 h of salt fog exposure, the best performing system incorporating AMPARMOR™ 2000 exhibited less than 1.5 mm of adhesion loss from scribe after 3500 h of salt fog exposure (Figure 4).

The concentration dependence of the corrosion resistance exhibited by systems incorporating AMPARMOR™ 2000 has important implications for designing anticorrosion solutions optimized for performance and cost. Remarkably, samples coated with systems incorporating AMPARMOR™ 2000 at a concentration of 5 wt.% did not fail until beyond 7000 h of salt fog exposure, representing life extension of close to 300% via the dynamic exposure/evaluation testing protocol. An identical system incorporating a green polyester topcoat as opposed to the white used in the evaluations discussed so far, exhibited an improvement over a leading epoxy powder coating of over 300% in the same dynamic exposure/evaluation testing protocol (Figure 5). Similar results were obtained for fusion bonded epoxy coating formulations.

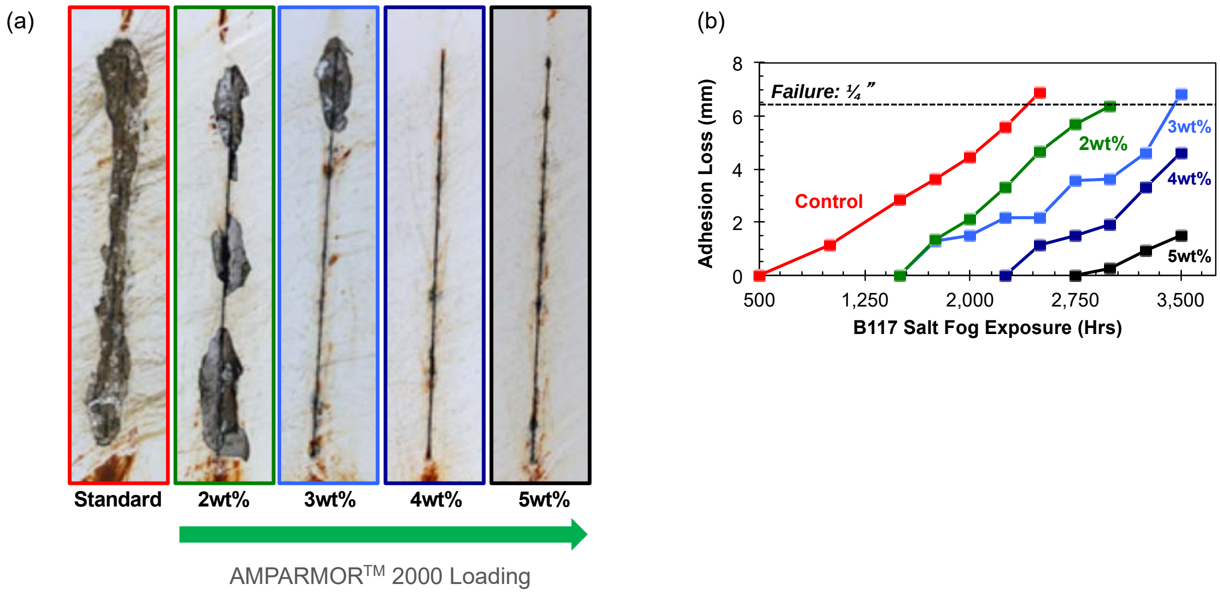


Figure 4. *Adhesion loss from scribe for coated B1000 pretreated CRS panels as a function of salt fog exposure. (a) Images of the scribed areas of the test panels after 2000 h. (b) Summary of adhesion loss as a function of time for coated substrates incorporating varying loadings of the AMPARMOR™ 2000 additive evaluated relative to the standard formulation (control).*

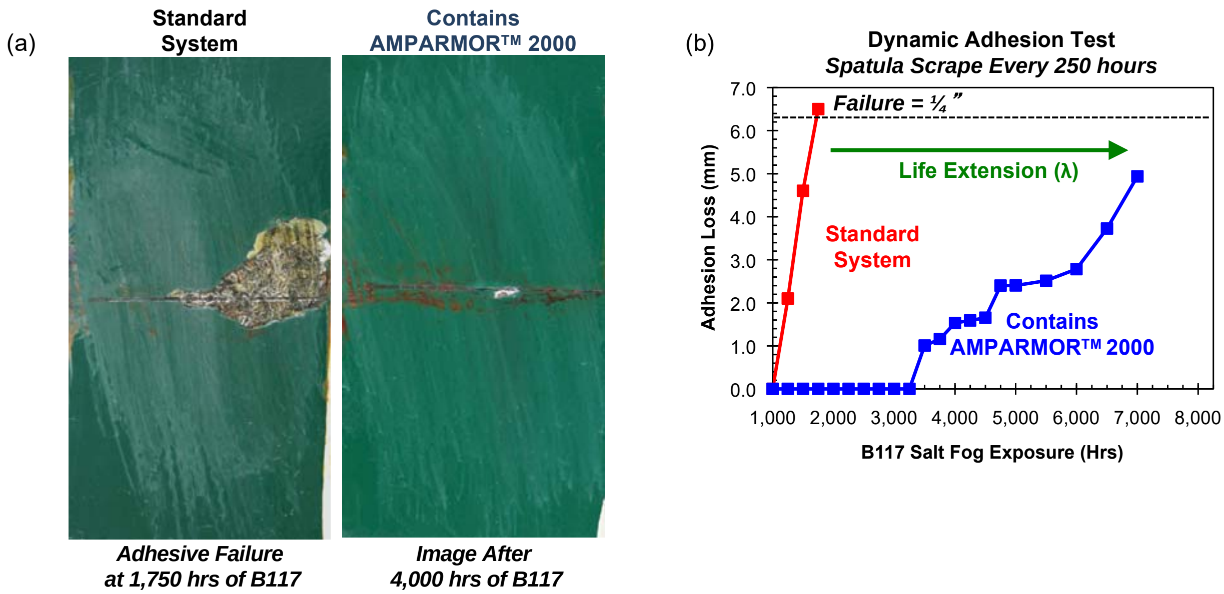


Figure 5. *Adhesion loss from scribe for coated B1000 pretreated CRS panels as a function of salt fog exposure. (a) Test panel images showing a comparison of adhesion loss from scribe for a powder coating system containing AMPARMOR™ 2000 relative to a leading epoxy primer (standard system). (b) Summary of adhesion loss as a function of time for coated substrates incorporating varying loadings of the AMPARMOR™ 2000 additive evaluated relative to the standard formulation (standard system).*

Liquid Coatings

AMPARMOR™ 2000 has also been evaluated in standard solvent-borne epoxy coatings and epoxy zinc-rich primers. In the case of the standard solvent-borne epoxy coating, the additive was evaluated in a polyamide/bisphenol A epoxy-based coating system. A comparison of the performance of the coating containing 5 wt.% of the AMPARMOR™ 2000 additive relative to the standard coating excluding the additive is provided in Figure 6. Blasted steel panels (SSPC-SP10) were coated using the standard commercially available epoxy coating as well as the version incorporating the AMPARMOR™ 2000 additive. After allowing the samples to cure and equilibrate at room temperature for 7 days, the samples were scribed using 156-micron and 186-micron scribe tools. The samples were then exposed to ASTM D4587, Cycle 2 conditions for 1000 h (alternating UV exposure at 340 nm Irradiance for 4 h at 60 ºC and condensation for 4 h at 50 ºC) followed by ASTM B117 (salt fog) conditions for 1240 h. As shown in Figure 6, the panels coated with the standard epoxy coating (control) exhibited significant adhesion loss around both scribes while the version incorporating 5 wt.% of the AMPARMOR™ 2000 additive exhibited practically no loss of adhesion following the sequence of accelerated testing described.

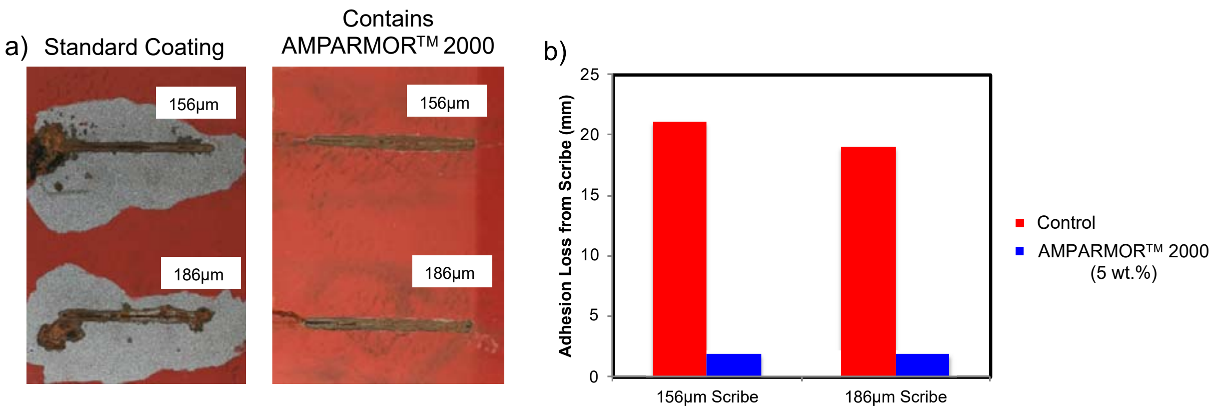


Figure 6. *Summary of performance of liquid epoxy coating for infrastructure protection. (a) Comparison of coated blasted steel substrates after ASTM D4587 (1000 h) and ASTM B117 (1240 h) exposures. (b) Summary of average adhesion loss from scribe for panels evaluated.*

Similar results were observed for blasted steel panels (SSPC-SP10) coated with three coat systems incorporating an epoxy zinc-rich primer as the first coat. The standard commercially available coating system was comprised of an epoxy zinc rich primer, an epoxy build coat and a polyurethane top coat (Figure 7a). The performance of this control system was tested relative to a version incorporating 4 wt.% of the AMPARMOR™ 2000 additive in the epoxy-zinc rich primer followed by the same epoxy build and top coats (Figure 7b). The panels were scribed using 186-micron and 500-micron scribe tools followed by salt fog (ASTM B117) exposure for 2000 h. The results obtained are summarized in Figure 8. While the control was observed to lose up to an average of 16 mm of adhesion on either side of the scribe for the 500-micron scribe, the version incorporating the AMPARMOR™ 2000 additive was found to exhibit less than 2 mm of adhesion loss at the same scribe width.

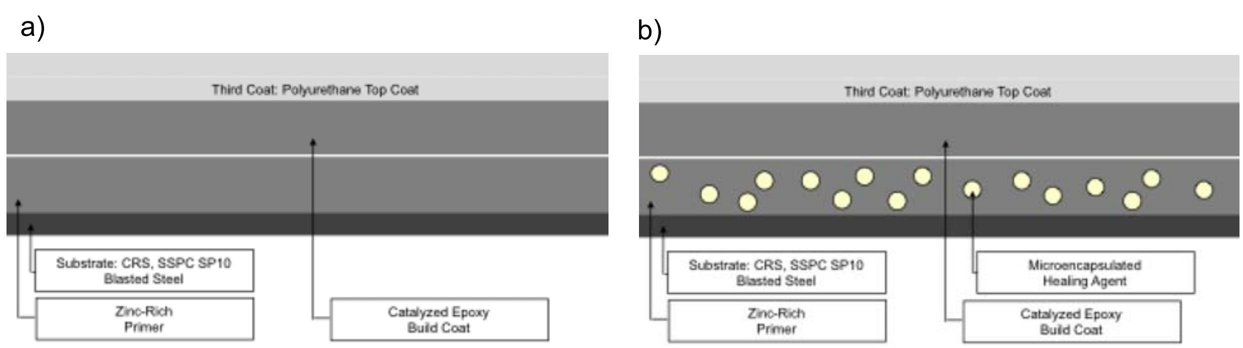


Figure 7. *Schematic showing three-coat system evaluated. (a) Standard control system. (b) Self-healing system incorporating AMPARMOR™ 2000 into the zinc-rich primer.*

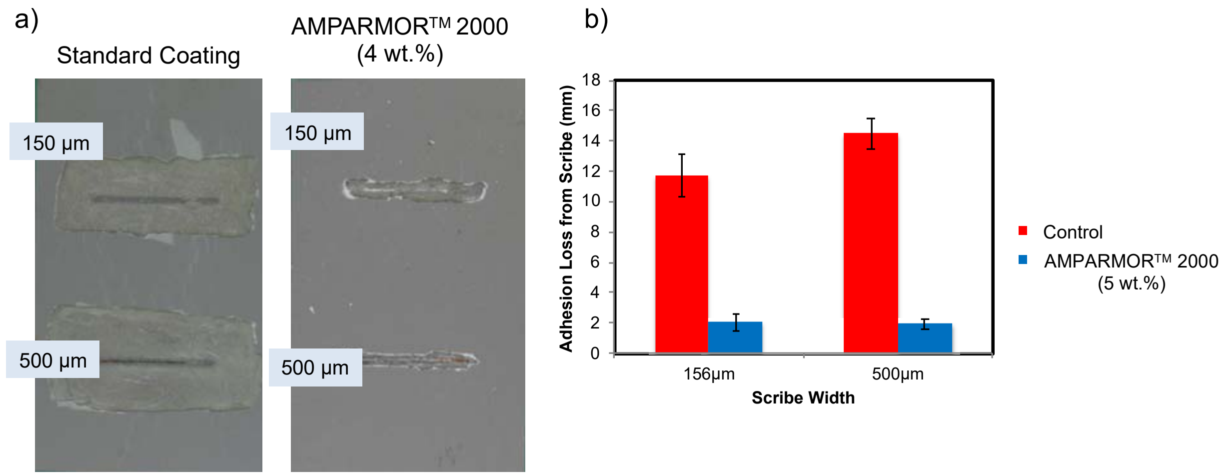


Figure 8. *Schematic showing three-coat system evaluated. (a) Standard control system. (b) Self-healing system incorporating AMPARMOR™ 2000 into the zinc-rich primer.*

Preparation for field trials in a combination of locations including Trinidad, Gulf of Mexico and North Sea are ongoing.

5. How can the innovation be incorporated into existing corrosion prevention and control activities and how does it benefit the industry/industries it serves (i.e., does it provide a cost and/or time savings; improve an inspection, testing, or data collection process; help to extend the service life of assets or corrosion-control systems, etc.)?

a) Self-healing additives incorporated into a protective coating arrest the propagation of corrosion. AMI's self-healing additive technology has demonstrated the ability to repair a damaged coating and prevent delamination, thereby preserving the anti-corrosion functionality of the coating. Moreover, this technology is autonomic, meaning it requires no mechanical or human intervention to provide healing at the site of damage. Self-healing additives for anti-corrosive coatings represent a qualitatively new technology that enables protective coatings to self-repair. When such coatings are damaged in service, the healing agent flows out of the microcapsules into the site of damage, where it forms a protective layer, passivates the damaged area and delays or prevents further corrosion of the underlying metal substrate. Consequently, formulating these microcapsules containing a self-healing agent into paint greatly extends the coating's serviceable lifespan by minimizing repaints and constant touch-ups.

b) Self-healing additives reduce the total cost of ownership. Performance improvements are an important consideration for any asset owner. However, the total cost of ownership is just as important. Hence, any discussion of an improved anticorrosion solution must consider the cost impacts of the solution. Based on financial models originally developed by NACE, AMI have recently developed financial models for multiple scenarios demonstrating how AMI's self-healing additives are cost-beneficial. Specifically, AMI's self-healing additives can lower the cost of maintaining assets in both moderate and extreme locations; from ubiquitous urban water towers to remote offshore oil rigs. In a recent case study published on the NACE Materials Performance online platform, AMI examined the economic benefit of using self-healing additives in both applications using the aforementioned calculations provided by NACE, where it was shown that end-users can reasonably save hundreds of thousands or millions of dollars if they can extend the lifetime of the paint by even just a few years. For example, it was demonstrated that a modest 25% increase in coating life time could translate to cost savings in excess of $5M for a single offshore oil platform if AMI's self-healing additive was used in a 3-coat system for improved corrosion protection in a C5-M environment (please see the published paper "*A New Standard in Corrosion Prevention: How Self-Healing Coatings Enable Significant ROI to End-Users*" for full details on the financial models as well as additional examples of significant cost-savings for other end-use applications at *www.materialsperformance.com/white-papers/autonomic-materials-inc*).

Furthermore, these massive cost savings take into account the added cost of the self-healing coating. Even if the cost of the coating doubles, the extension in serviceable lifespan more than covers the increased price. Fundamentally, the self-healing additive effectively makes every gallon of paint less expensive. It's also worth noting that the cost of the coating itself is typically only a fraction of the total costs associated with the total paint maintenance sequence – particularly for structures that present logistical difficulties, like offshore oil platforms. As such, the extended lifespan continues to pay dividends throughout the asset's lifespan by:

- Preventing corrosion of the underlying substrate;
- Maintaining adhesion to the substrate even after coating damage occurs;
- Providing additional protection in areas of marginal coating application and difficult-to-inspect areas;
- Reducing environmental impact by lowering VOC emissions released;
- Reducing material and labor costs as the frequency and size scale of recoating is reduced;
- Reducing business disruption and lost opportunity costs; and
- Increasing overall asset lifetime because of longer lasting coatings.

In short, any paint system for a big structure – regardless of composition, complexity, environment, or surface preparation – will see improved service life and cost effectiveness when self-healing additives are used in a protective coating system.

6. Is the innovation commercially available? If yes, how long has it been utilized? If not, what is the next step in making the innovation commercially available? What are the challenges, if any, that may affect further development or use of this innovation and how could they be overcome?

Yes, the innovation is commercially available. The first commercially available self-healing coating containing AMI's additives was launched in 2017 by a large manufacturer of protective paints and coatings. In addition to the originally targeted use for industrial maintenance applications, this self-healing coating is also currently at various stages of field trials for specification in the oil & gas industry as part of multi-coat self-healing protective systems for some of the most demanding environments, including C5-M.

AMI is also actively engaged in product development with other major coatings suppliers and end-users with 2018 - 2021 target product launches, as well as additional development work underway in adhesives and sealants expansion markets.

7. Are there any patents related to this work? If yes, please provide the patent title, number, and inventor.

- Self-Healing Agent Formulations Containing Liquid Corrosion Inhibitors; 9,279,043; Gerald O. Wilson
- Dispersion of Microcapsules for Self-Healing Applications; 9,771,478; Gerald O. Wilson, Subramanyam V. Kasisomayajula, Ryan T. Blanchette.
- Improved Zinc-Rich Primers via Microencapsulated Healing Agents; Application No. 15/948,708; Gerald O. Wilson, Subramanyam V. Kasisomayajula, Christopher R. D. Dayton.