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13. SUPPLEMENTARY NOTES					
14. ABSTRACT The goal of this project is to develop a primer additive that mimics the self-healing ability of skin by forming a polymer scar across scratches. Designed to work with existing military grade primers, Polyfibroblast consists of microscopic, hollow zinc tubes filled with a moisture-cured polyurethane-urea (MCPU). When scratched, the foaming action of a propellant ejects the resin from the broken tubes and completely fills the crack. No catalysts or curing agents are needed since the polymerization is driven by ambient humidity.					
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Award Information

Award Number	N00014-09-1-0383
Title	Polyfibroblast: A Self-Healing & Galvanic Protection Additive
Principal Investigator	Dr. Jason J. Benkoski
Organization	The Johns Hopkins University Applied Physics Laboratory

Technical Section

Objective

Corrosion costs over \$300 billion per year in the US, and as much as \$4 billion per year to the Navy alone. The most cost effective method for preventing rust is to paint the surface. This protection, however, is only temporary, as paint inevitably develops scratches. The ability to make more durable coatings must be balanced against the convenience of spray painting. The latter requirement effectively limits the feasible options to polymeric coatings, which, in turn, constrains the maximum achievable wear resistance. The objective of this program is to achieve revolutionary gains in corrosion protection by developing self-healing, damage tolerant coatings, rather than pursue incremental gains in damage resistance.

Approach

JHU/APL has developed Polyfibroblast, a paint additive for commercial-off-the-shelf (COTS) primers that confers self-healing and galvanic protection capacity to the primer (Figure 1). Polyfibroblast consists of paint-filled microcapsules and zinc powder. **It has been shown to prevent rusting for 6 weeks in a salt fog chamber. Standard CARC coatings rust within hours, and zinc-rich CARC coatings rust within one week by comparison (Figure 2).** Polyfibroblast delivers dramatic performance gains without requiring retooling, retraining, reformulation, or significant added cost.

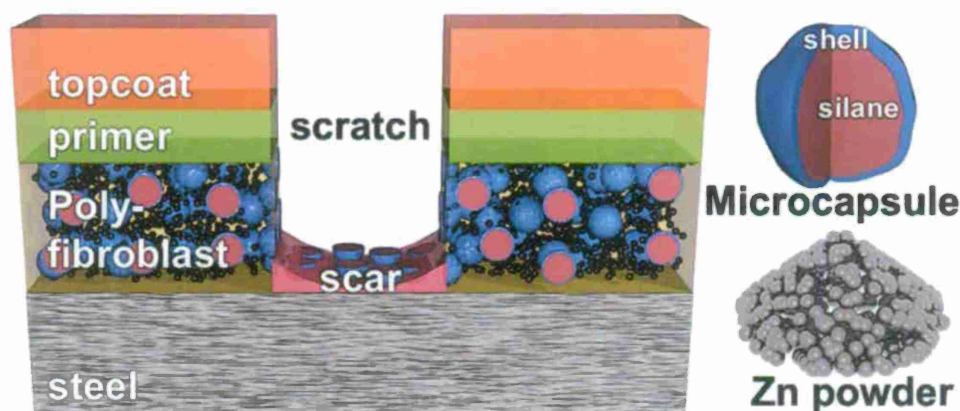


Figure 1. Polyfibroblast contains fresh paint encapsulated in polymer shells plus Zn powder. When scratched, resin from the broken microcapsules fills the crack to form a polymer scar. Zn powder supplies galvanic protection in the event of incomplete healing.

Progress

The corrosion protection of Polyfibroblast self-healing paint was optimized by adjusting three parameters: silane type, silane concentration, and zinc dust loading. Experiments revealed that the three variables are interdependent and must be varied simultaneously to determine the optimum formulation. Figure 2 displays several of the best performing formulations. Note the exceptional performance of Polyfibroblast across a wide range of parameter space. This variety is perhaps most impressive in Figure 3, where over 20 formulations display major performance advantages over the CARC and zinc-rich CARC controls. In general, the combination of zinc powder and microcapsules performed better than either alone. Silanes that formed monolayers (octadecyltrimethoxy silane, OTS) tended to work best at high silane concentration and high zinc loading. Silanes that operated as wetting agents (glycidoxypropyl-trimethoxy silane, GPS) worked best at low silane concentration and low zinc loading.

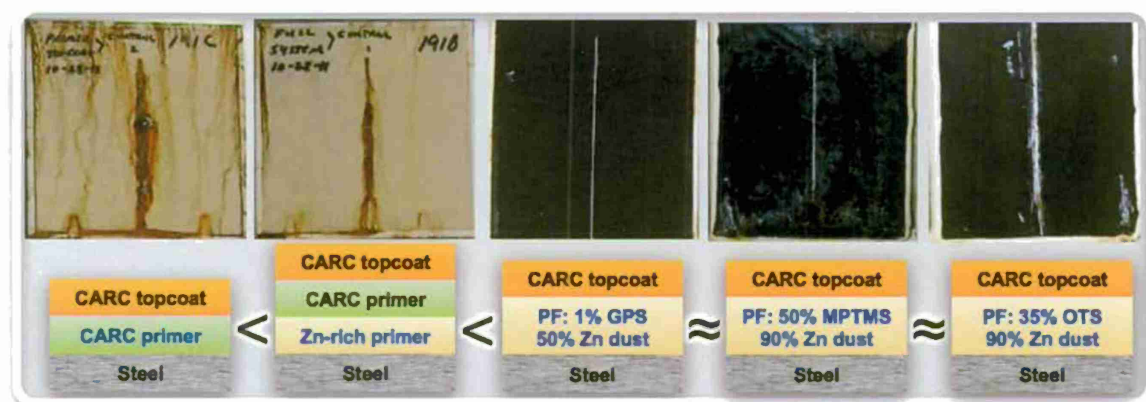


Figure 2. 6 week salt fog panels compared for standard CARC coatings and Polyfibroblast.

Electrochemical Impedance Spectroscopy (EIS) further supported these findings by providing direct evidence of self-healing. Figure 4 shows that the impedance of the original coating was on the order of 100,000 Ω , but immediately following the scratch, it would fall to about 100 Ω . The self-repair mechanism would then restore the impedance to within an order of magnitude of the original value within 48 hours. Together with the galvanic protection of the zinc dust, corrosion within the scratch is completely arrested.

Based on the salt spray, moisture resistance tests, and electrochemical impedance spectroscopy, there was no clear winner in terms of self-healing and corrosion protection. *However, 65% OTS microcapsules with a 90% zinc dust loading provide the best option when additional factors such as cost, shelf life, and environmental risks are taken into account.*

OTS works best at low loading: Since it forms a molecular monolayer, a small volume spreads across a large area. The low volume fraction offsets the extra cost of the microcapsules and benefits the mechanical properties of the primer. **OTS hydrolysis is slow:** Polyfibroblast microcapsules degrade by reacting with water and solidifying prematurely. OTS microcapsules show no loss of performance after one year of storage. **OTS has a lower environmental and health risk:** OTS formulations are somewhat unique for fact that they work in the absence of any polymer film. Unlike other silanes that must work in tandem with isocyanate precursors, pure OTS will passivate exposed steel. By eliminating toxic components such as monomeric IPDI, OTS microcapsules can be handled in the open with little risk to health or the environment.

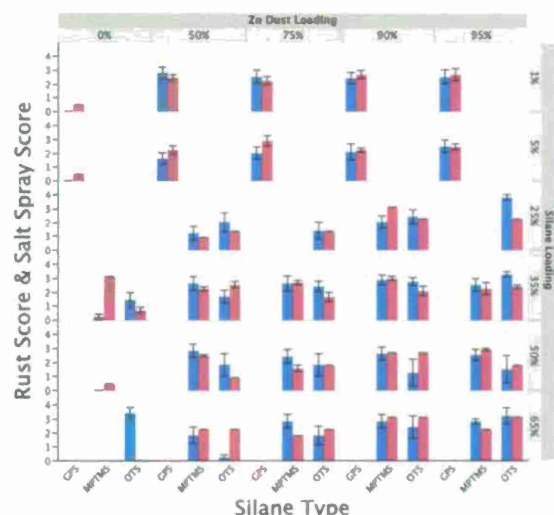


Figure 3. Plot moisture resistance rust score (blue) and salt spray scores (red) for samples prepared in FY12. For comparison, the zinc-rich control primer averaged a rust score of 2 and a salt spray score of 3. 65% OTS with 90% Zn dust was chosen as the best formula.

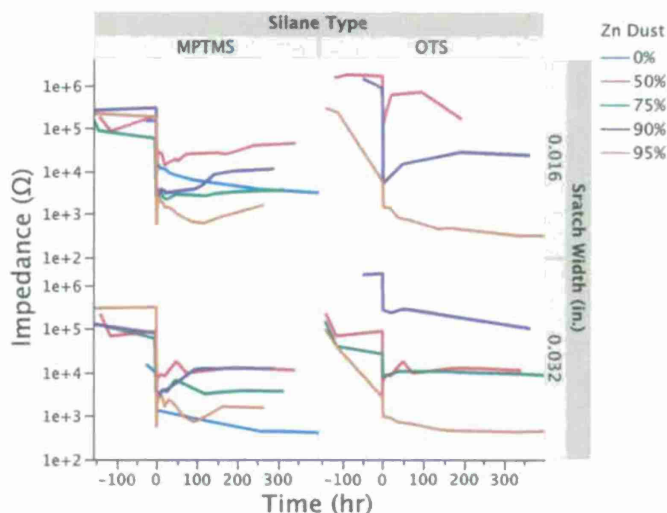


Figure 4. Plot of the magnitude of complex impedance at 0.36 Hz versus time for Polyfibroblast coatings. Impedance spectroscopy directly observes self-healing in real time, and it shows recovery to within an order of magnitude of the original impedance.

Cumulative Statistics

Documentation / Publications

M. W. Patchan, L. M. Baird, Y.-R. Rhim, E. D. LaBarre, A. J. Maisano, and J. J. Benkoski "Liquid-Filled Metal Microcapsules," *ACS Applied Materials & Interfaces* **4** (2012) 2406-2412.

L. M. Baird, M. W. Patchan, J. L. Breidenich, Y.-R. Rhim, E. D. LaBarre, A. J. Maisano, R. M. Deacon, E. Ott, J. J. Benkoski, "Self-Healing Coatings with Galvanic Protection," *PCI Magazine*, (2012) March Issue.

Conference presentations/proceedings

A. J. Maisano, R. Srinivasan, M. W. Patchan, L. M. Baird, E. D. LaBarre, J. J. Benkoski, "Environmental and Temporal Characterization of a Self-Healing Coating with Galvanic Protection," Pacific Rim Meeting on Electrochemical and Solid-State Science, Honolulu, HI, Oct 7-12, 2012.

Invention disclosures/patents

Nonprovisional Patent Application, "Self-Healing Coatings," August 29, 2012. USPTO patent application number 2011-0293958-A1

Students/Postdocs supported by this award

N/A

Other noteworthy recognition

- Received praise and interest from Michael Halloran, Science and Technology Director for the Program Executive Office of Land Systems for the US Marine Corps
- This program will receive development support for transitioning the self-healing paint technology to the US Marine Corps variant of the Joint Light Tactical Vehicle (JLTV)