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# POLYFIBROBLAST: A SELF-HEALING AND GALVANIC PROTECTION ADDITIVE

*Progress Report #3*

N00014-09-1-0383

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Reporting Period: February 28, 2011 through March 28, 2011
Date of Report: March 28, 2011

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# 1 Summary

APL has begun polarization studies to characterize the corrosion resistance afforded solely by the Ni:Zn alloy. APL has also demonstrated the ability to plate a Zn-rich alloy that is expected to have > 60% Zn by atom fraction. Lastly, PPG has developed a method for the scale up of the emulsification process that simultaneously results in reduced particle size.

# 2 Project Goals and Objectives

The next major milestone is to determine the Ni:Zn alloy that provides the best galvanic protection to steel based on electrochemical characterization. According to the current research plan, this objective is due by the end of April. The following milestone is the ability to heal 1/32" scratches by month 5 (2 months from now). APL is currently working to encapsulate wetting agents to improve resin spreading upon microcapsule rupture.

# 3 Key Accomplishments

## 3.1 Zn-rich Alloy

A patent search uncovered an electroless plating recipe containing 96.5% Zn by mole fraction. According to the patent, this recipe may be modified to obtain Ni:Zn alloys consisting in excess of 60% Zn. Unlike previous recipes, this formulation requires high pH (12.2 – 12.6) and operates down to even lower temperatures (20°C – 70°C). This recipe was also notable for the rapid rate of metal deposition relative to previous electroless methods.

Figure 1 shows the first attempt at plating liquid-filled microcapsules. Note the relatively low coverage of metal. In subsequent attempts, very thick metal layers could be plated on glass through greater attention to the catalyst deposition, and through higher plating temperatures. Characterization of these films is currently underway.

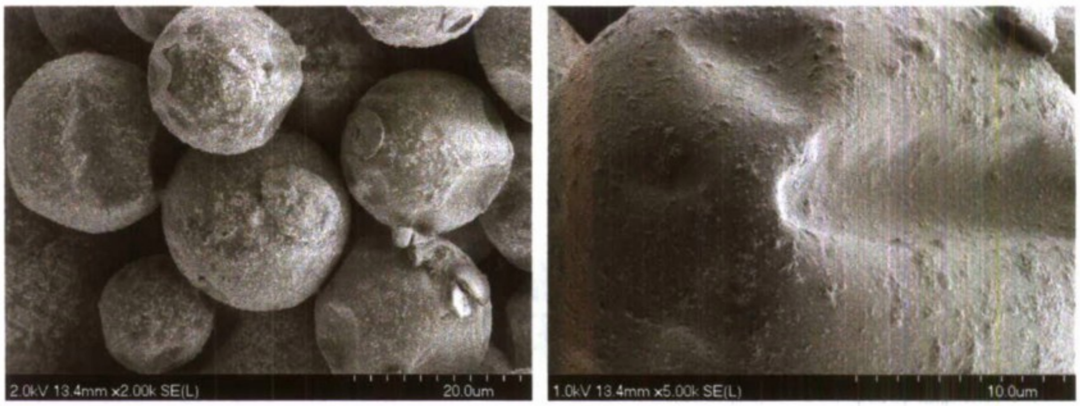



***Figure 1:*** *SEM images of microcapsules plated with a 96.5% Zn plating bath. The relatively low surface coverage was obtained at room temperature. Plating at 70°C on glass resulted in a thick metal foil.*

## 3.2 Electrochemical Characterization

Using electrochemical techniques, we characterized the corrosion protection properties of the nickel-zinc alloy coatings on urethane microcapsules dispersed polyurethane on A1008 steel. The techniques included measurements of open circuit voltage (OCV), cathodic protection (CP) current, linear polarization, logarithmic polarization and ac impedance. Characterizations are being made in two different electrolytes, and under two different concentrations of dissolved oxygen (in the electrolyte). The electrolytes are aqueous solutions of 0.1 M $Na_2SO_4$ and 0.1 M NaCl; the former helps to characterize the CP capabilities under relatively benign or noise-free conditions, since $Na_2SO_4$ is a much less corrosive than NaCl. Similarly, the oxygen concentrations are deaerated and un-deaerated; the former being less corrosive than the later therefore providing a manageable environment for characterization purposes. We are finished characterization studies in 0.1M $Na_2SO_4$ solutions; we are just about ready to start characterization in 0.1M NaCl.

Note that in addition to characterizing the steel under CP using the Ni-Zn coatings on urethane microcapsules, we also tested the steel against nickel and zinc wires in absence of polyurethane. The results established the extent of voltage polarization and current flow that each element effected on A1008 steel, and provided a qualitative trend to the direction and magnitude of the anticipated behavior of the alloy coatings on the microcapsules. The studies so far have yielded valuable information on the direction and amplitude of pure nickel, pure zinc and one 25% zinc alloy coated on microcapsules. Analysis of the data is still underway and will be included in the next monthly report.

## 3.3 Incorporating Wetting Agent into Formulation

Wetting agents will be incorporated into the Polyfibroblast formulation to improve the spreading of the polyurethane resin following the formation of a scratch. If properly designed, the wetting agents should make it possible to spread a continuous, albeit thin, polymer layer across even wide scratches. Continuous films are necessary to provide a moisture barrier and prevent corrosion.

We have so far experienced limited success in incorporating the wetting agent directly into the polyurethane precursor resin. The main difficulty arises from the fact that the wetting agent is water-soluble. The only way to make the surfactant insoluble is to use high temperatures and high salt concentrations. Unfortunately, these conditions also lead to unwanted internal polymerization. The internal polymerization frequently results in solid polymer spheres rather than liquid-filled microcapsules.

Since the wetting problem needs to be solved in the next two months, we will try a different approach in which the wetting agent is encapsulated separately in its own microcapsule. These wetting agent-filled microcapsules will then be mixed in with the normal polyurethane resin-filled microcapsules prior to making a paint. The tradeoff is the potential lack of mixing between the wetting agent and resin during the formation of a scratch.

## 3.4 Rotor-Stator Mixer

To scale up the current batch size, PPG has begun using a rotor-stator mixer as an emulsifier. Known more commonly as a Ross Mixer, this equipment emulsifies immiscible liquids through a combination of blades or teeth rotating rapidly in close proximity to a set of stationary blades or teeth. The current piece of equipment can handle up to 1-gallon batches. Larger Ross Mixers are available, and some are designed to operate continuously for enhanced throughput.

The rotor-stator mixer has the additional advantage of producing finer emulsions. The current mixer has settings from 1 to 10, and a setting of 2 already produces smaller particles than are possible on the mechanical mixer at APL. A setting of 4 produced particles with an average diameter around 10 µm, which is nearly identical to the 7 µm average particle size of the zinc filler in MIL-P-26915. The full data set is shown in Figures 2 and 3 below.

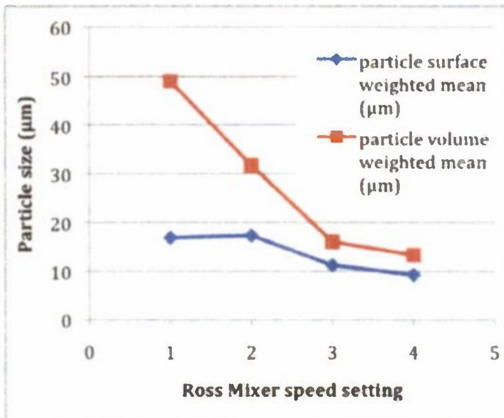



***Figure 2:*** *Plot of particle size versus mixing speed for the rotor-stator mixer. Volume weighted particle sizes ranged from 50 down to 10 µm. For comparison, the smallest size attained using an IKA mechanical mixer was 37 µm.*

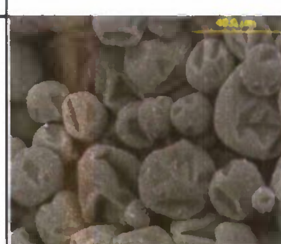
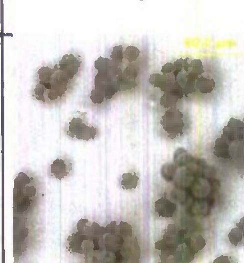
| 11-JS-015 | 11-JS-012 | 11-JS-011 | 11-JS-017 |
|---|---|---|---|
| 1 | 2 | 3 | 4 |
|  | Failed for plating |  |  |
| After plating | | After plating | After plating |

***Figure 3:*** *SEM micrographs of microcapsules prepared at different speeds using the rotor-stator mixer. The speed setting is given above each micrograph.*

### 3.5 Contributed Talk at American Physical Society March Meeting

Marcia Patchan presented a talk titled, "Self-Repair of Polymer Films Through Monomer-Filled Ni-Zn Microcapsules," at the American Physical Society March Meeting in Dallas, TX.

## 4 Next Steps

### 4.1 PPG Synthesis

Having successfully demonstrated the ability to synthesize liquid-filled metal microcapsules, PPG will be moving towards the production painted panels. They will compare the MIL-P-26915 resin to several other formulations manufactured by PPG. They will also continue to increase their batch production size.

### 4.2 APL Property Characterization

APL will continue polarization studies to evaluate the level of galvanic protection provided by the range of Ni:Zn alloys produced by electroless deposition. We will also work to encapsulate wetting agent by itself, since this synthesis appears to be more feasible than trying to co-encapsulate the agent with the polyurethane precursor.