**Title**: Polyfibroblast: A Self-Healing and Galvanic Protection Additive

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**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.

**Subject Terms**

corrosion protection, self-healing, coatings, polymers
POLYFIBROBLAST: A SELF-HEALING AND GALVANIC PROTECTION ADDITIVE

Progress Report #15

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1 Summary

A new microcapsule recipe has been developed that replaces the Gum Arabic emulsifier with silica nanopowder. The silica nanopowder reduces microcapsule aggregation, strengthens the shell, and decreases the permeability of the shell to water, increasing shelf life. PPG is scaling up the new process and comparing properties with the old microcapsules such as pot life and corrosion protection.

2 Project Goals and Objectives

With the conclusion of the field test, all major project goals have been delivered. The remaining month will be spent developing quality control measures for the manufacturing process.

3 Key Accomplishments

3.1 New Microcapsule Formulation

A recurring topic in the feedback from PPG was that the Gum Arabic emulsifier appeared to be the cause of microcapsule aggregation. PPG spent great effort to purify the excess Gum Arabic. When they did so, they observed an improvement in the flow properties of the dry microcapsule powder.

An alternative strategy for stabilizing an emulsion is to form a Pickering emulsion (Fig. 1). A Pickering emulsion is formed when small particles embed themselves at the oil/water interface. The particles protrude from the oil droplets, preventing the oil from making intimate contact when the droplets collide. Effectively, the particle protrusions create a repulsive force between droplets and stabilize the emulsion.

An added benefit in our case is that the particles eventually embed themselves within the polymer shell of the microcapsule. Since glass is much harder and stronger than the polymer, the nanoparticle coating improves the overall mechanical properties of the shell. The polymer shell essentially becomes a glass-filled composite. The second advantage to the silica nanoparticles is that they prevent the diffusion of water. While water can still diffuse through the polymer matrix, it must travel through a much more tortuous path to reach the moisture-sensitive silane inside.

Figure 2 shows that the microcapsules indeed have silica nanoparticles decorating the outside of the polyurea shell. They appear roughly the same in appearance as before, except they are less prone to aggregation. One can now obtain a free flowing powder by heating to 70°C for two hours, whereas before caking was more difficult to remove. The only potential drawback at this time appears to be the fact that the silica holds onto water more strongly than the polyurea. Overall, this hygroscopic nature means that the drying methods need to be more aggressive.
Water removal is critical to obtaining long pot-life in the moisture-cured polyurethane paints that we are using.

Figure 1: Schematic of microcapsule formation using a Pickering emulsion.

Figure 2: (left) Microcapsules formed with silica nanopowder as the stabilizer incorporate the silica into the outer shell. (center) The microcapsules formed this way are less prone to agglomeration. (right) They form free-flowing powders after only minimal heating and aggregation.

3.2 Scale up of New Formulation

A 4kg batch of the old microcapsule recipe was prepared and will be tested for potlife and performance. The capsules will be stored under nitrogen for use as backup material for future field tests should the new Pickering emulsion based capsules prove difficult to make by the continuous process or be lacking in potlife or performance. Two batches of the new Pickering emulsion based capsules have been prepared. The Pickering approach will require modification of the standard method to higher shear so that the correct particle size is obtained. The silica containing capsules appear to be more resistant to clumping and are easier to add to paint when properly dried, but they appear to be harder to dry. Salt fog and Cyclic testing of the old recipe is underway. Testing of a Pickering capsule based zinc rich is expected to begin shortly.

3.3 Experimental Strategy

Our work during this report period has concerned itself with the preparation of sufficient microcapsules to conduct future tests and to understand the effects of preparation, washing and drying conditions on particle performance. Our strategy has been to devote a relatively small
amount of effort to the preparation of a large batch of the Lejeune type capsules (with Gum Arabic) in order to have these capsules in reserve for future tests if the Pickering emulsion type capsules prove to be unsuitable. A portion of these capsules will be used to thoroughly characterize the batch and to determine the expected pot-life and performance of the corresponding moisture cured zinc rich paint. The bulk of our efforts have concerned themselves with using the continuous process approach to produce the Pickering emulsion type capsules and then to determine the corresponding expected pot life and performance.

3.4 Outline of Work Completed

1. Lejeune Type Capsules (Old recipe with Gum Arabic)
   a. Different drying conditions studied.
      i. Control Particles, no drying - 5.41% H2O
      ii. Dry at 70°C to constant weight – 0.21% H2O
      iii. Dry at 110°C to constant weight – 0.16% H2O
   b. Capsules Washed in Solvent (Solvesso 100)
      i. Washing did not affect %OTS
   c. Alternative Preparations
      i. Pre-emulsion done with Ross Mixer instead of stirrer. – Narrower particle size distribution was obtained and core composition remained the same.
      ii. All emulsion done in Ross Mixer followed by crosslinker addition. – Results similar to standard preparation.
   d. Synthesized a 4kg batch of capsules sufficient for future testing and thorough evaluation and testing.
      i. Capsules being isolated and dried. Testing and evaluation will begin soon.
   e. Additional testing
      i. Enhanced Lejeune type zinc rich primer and control panel series prepared and placed in Salt Fog – 1000 testing.
      ii. Enhanced Lejeune type and control series with epoxy primer was prepared and submitted for GMW 120 cyclic corrosion testing.
      iii. Patti Adhesion tested for Lejeune type enhanced zinc rich and control zinc rich coating over smooth cold rolled steel panels and blasted cold rolled steel panels. Results indicate a marginal adhesion (c.a. 200psi) for both enhanced and control zinc rich primers on smooth steel but good adhesion (c.a. 600 to 800psi) over the blasted substrate.
      iv. Enhanced Lejeune type zinc rich applied to horizontal and vertical substrates to determine if capsule orientation is influenced primarily by gravity or surface energy.

2. Pickering Emulsion Based Microcapsules
   a. Sigma Aldrich Silica Fingerprinted – Samples submitted for analytical testing to characterize the material so that an equivalent industrial product can be used and other significantly different silicas can be explored.
   b. Synthesized a batch of Pickering emulsion based capsules
Using standard continuous process conditions. Particle size distribution by light scattering shows a volume weighted mean of 120 microns, much larger than standard. Core content and SEM images in process.

Using higher shear rotor-stator. Analysis of particles underway but particles appear smaller and take longer to settle after mixing.

1. Filtration slower than Lejeune material but new capsules dried to a free-flowing powder.
2. Powder readily sieved through a 106 micron mesh screen with significantly less loss than Lejeune capsules.
3. Capsules dried at 110°C for 4 hours easily stir into zinc rich moisture cured primer without being slurried with solvent first. Paint made from these particles lasted for greater than 72 hours without gelling.

4 Next Steps

4.1 Quality Control

PPG will spend the final month of the FY12 project implementing quality control measures into their manufacturing process. We will work together to develop protocols and measurements that will help us to quantify various aspects of the microcapsules that will, in turn, help us to qualify the material for future use.