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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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POLYFIBROBLAST: A SELF-HEALING AND GALVANIC PROTECTION ADDITIVE

Progress Report #16

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1 Summary

Synthesis of the new silica-coated microcapsules has been improved to decrease the diameter to the same range as the old Gum Arabic recipe. Recent experiments appear to confirm our suspicion that the residual moisture on the microcapsules directly controls the pot life of the primer. With the addition of a water scavenger, the pot life of the large batches has been increased to two weeks.

2 Project Goals and Objectives

All major tasks and milestones for phase III have been completed.

3 Key Accomplishments

3.1 Refinement of Silica-Coated Microcapsules

1.2 kg of microcapsules has been prepared using the old Gum Arabic technique and are stored under nitrogen for later use. Another 1 kg batch of silica-coated microcapsules has been prepared at 7000 rpm in an effort to produce material in the 20 to 30 μm range. These microcapsules have been sieved, dried and submitted for core analysis and SEM imaging. Using the 34 μm silica-coated microcapsules made last month we have studied the effect of drying and moisture scavenging on pot life. Extensively dried pickering microcapsules give a pot life of about 3 days without the addition of a moisture scavenger. Addition of 1% pTSI (p-toluenesulfonyl isocyanate) extends the pot life to greater than 13 days.

3.2 Quality Control Efforts

Control NCP zinc rich primer and microcapsule enhanced primers were painted on as-received Cold Rolled Steel to evaluate whether they meet the MIL-P-26915 specification. Subjecting these panels to 15 cycles of GMW14872 testing has begun to show failures with no clear cut differences between the control and the enhanced primers. Such adhesion issues are common when the surface has not been treated properly. Due to the low polymer content, the MIL-P-26915 primers generally require a roughened surface, such as one would achieve via sand blasting or zinc phosphate treatment.

As expected, the same coatings applied to sand blasted steel panels still look good after 15 cycles for all test systems. Work is underway to find a more rapid screening technique for self-healing properties and to understand what conditions promote the healing in the scribe.

3.3 Experimental Strategy

Our work in March has concerned itself with the preparation of sufficient microcapsules of the Pickering type to understand the factors that shorten the pot life of the enhanced zinc rich primer and to mitigate them. Work is also underway to enable a more rapid screening of coatings for the self-healing capacity and to better characterize our microcapsules, the optimum conditions for zinc rich application, and healing after damage.

3.4 Outline of Work Completed

1. Microcapsules Formed using Gum Arabic Emulsifier
    a. Microcapsules have been prepared, filtered, washed and partially dried and sieved and then dried again followed by storing under nitrogen for future use and characterization. We intend to collect qualitative data to conclusively demonstrate that the new Pickering emulsion method produces microcapsules with superior properties.

2. Silica-Coated Microcapsules
    a. Synthesized 1 kg batchs of Pickering emulsion based capsules
        i. Using higher shear rotor-stator
            1. SEM images of the microcapsules processed at 6000 rpm give a size of 34.0 ± 17.3 µm.
            2. Second batch processed at 7000 rpm in order to bring particle size into 20 µm range. These particles will be sent for core analysis and SEM imaging.
    b. Shelf Life Testing for NCP Zinc Rich Primer formulated with standard level of
        i. Microcapsules dried at 120°C for 4 hours to moisture contents of less than 0.2% water as measured by Karl Fisher Titration
            1. Without moisture scavenging additive – 3 days before gelling
            2. With 1% pTS1 moisture scavenger – 13 days still fluid, paint reduced, sprayed out, and under evaluation.

3. Testing
    a. A JHU / APL panel series was prepared and put into 1000 hours salt spray testing and submitted for 120 cycles GMW14872 cyclic corrosion testing.
    b. Series with Gum Arabic and silica-coated microcapsule enhanced zinc rich NCP primer submitted for 120 cycles GMW14872 cyclic corrosion continued in test.
        i. At 15 cycles Cold Rolled steel panels have begun to show failures with no clear cut advantage for systems which contain microcapsules over the control standard NCP primer.
        ii. At 15 cycles all Blasted Steel panels are doing well.
    c. Efforts are underway to allow for rapid screening of candidate systems and for the QC of batches of microcapsules.

i. Surface Resistivities of Control NCP and Enhanced NCP primers are $5x10^6$ and $11x10^6$ Ohm/sq respectively indicating we may be able to use simple enamel rater instrumentation to evaluate self-healing.
    1. Enamel rater evaluation underway.
    2. 1 μm films of OTS prepared on Cold Rolled Steel and Blasted Steel panels and will be tested for corrosion resistance and cure times in moist air with and without added cure catalysts.