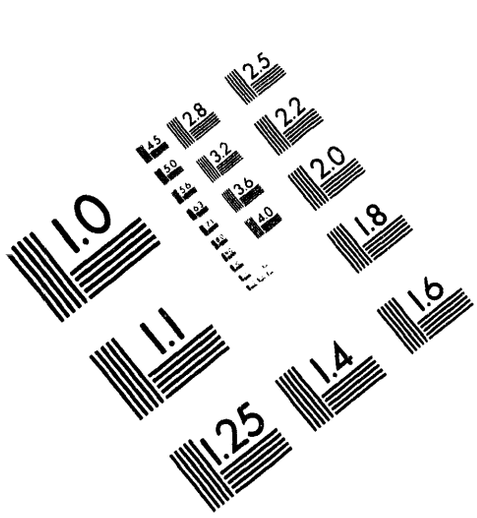

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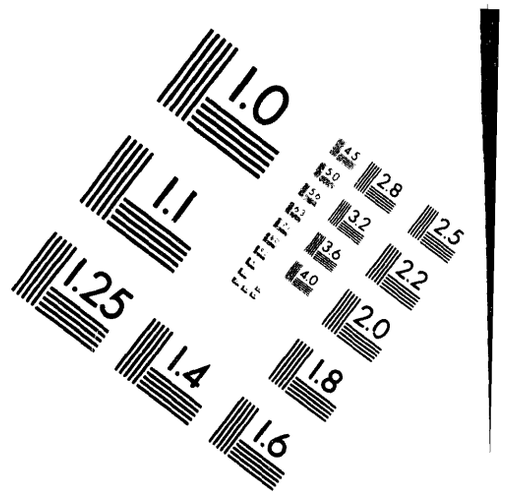

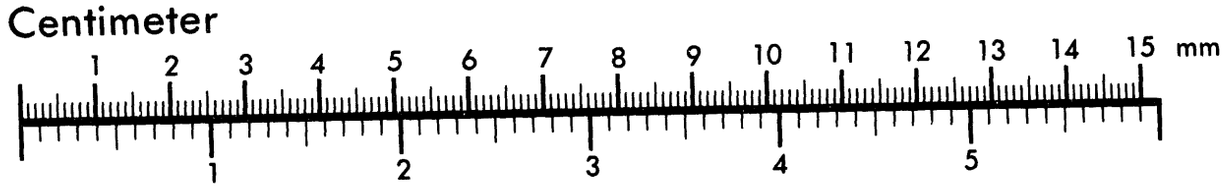

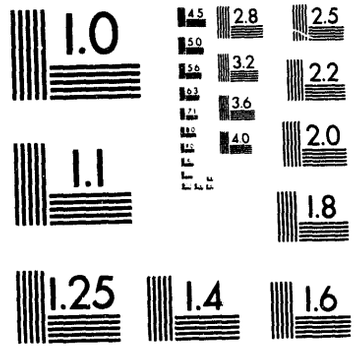

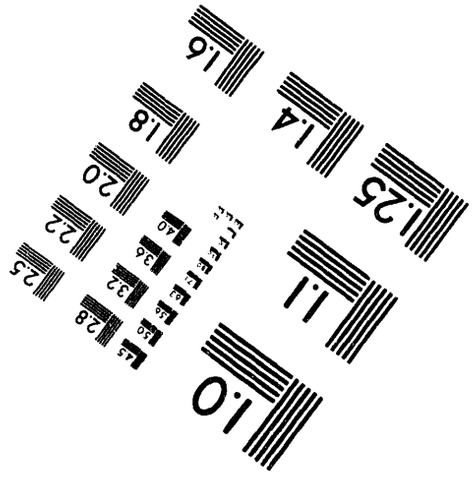

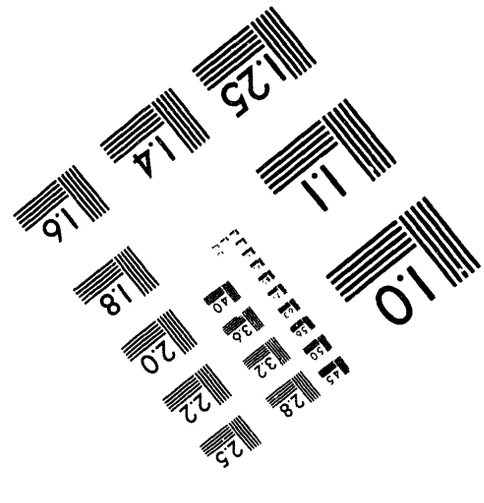

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Title: CONDUCTING POLYMERES AS CORROSION RESISTANT COATINGS

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CONDUCTING POLYMERS AS CORROSION RESISTANT COATINGS

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INTRODUCTION

Although the majority of top coatings used for corrosion protection are electrically insulating, previous workers have proposed using an electrically active barrier for corrosion control[1]. The most effective corrosion resistant undercoatings in use today are based on chromium compounds. Coatings based on other materials will need to replace these coatings by the turn of the century because of environmental and health concerns. For this reason we have begun an investigation of the use of conducting polymers as corrosion resistant coatings as an alternative to metal-based coatings.

Conducting polymers have long been considered to be unsuitable for commercial processing[2], hindering their use for practical applications. Research in the field of electrically conducting polymers has recently produced a number of polymers such as polyaniline and its derivatives[3] which are readily soluble in common organic solvents. Our coating system, consisting of a conducting polyaniline primer layer, topcoated with epoxy or polyurethane, has been evaluated for corrosion resistance on mild steel substrates. In this paper we report the results of laboratory testing under acidic and saline conditions and the results of testing in the severe launch environment at the Beach Testing Facility at Kennedy Space Center. The launch environment consists of exposure to corrosive HCl exhaust fumes and the salt spray from the Atlantic Ocean

EXPERIMENTAL

The emeraldine base of polyaniline (PAn-EB) was prepared by oxidation of aniline in hydrochloric acid by ammonium persulfate using standard methods, followed by treatment with 3 % NH_4OH for 2 hours.[4] Mild steel samples were coated with 5 wt% PAn-EB solutions in N-methylpyrrolidinone (NMP) using spray coating techniques resulting in 1-2 mil thick coatings from building up of multiple coating layers. The undoped polyaniline coating was dried at 100°C for 14 hours. The coated samples were doped by immersion in 0.1 M solution of dopant in tetrahydrofuran (THF) solutions for 14 hours followed by rinsing with THF. We have evaluated p-toluenesulfonic acid, tetracyanoethylene, and zinc nitrate as dopants. After doping the test samples, a topcoat of epoxy or polyurethane was applied by dip coating or spray coating followed by temperature cure for the epoxy coating or drying for the polyurethane coatings. The epoxy topcoat used for laboratory tests was obtained from Ciba-Geigy as Bisphenol A GY 2600 resin cured with a cycloaliphatic / aliphatic amine hardener XU265. The Ciba Geigy Bisphenol A system was chosen because of its reported resistance to acid in a study of materials for coating the interior of stacks emitting sulfur dioxide in power plants[5]. The polyurethane coating used for the beach site tests was the DeVoe Devethane 379. The polyurethane topcoat was chosen for the beach site tests because it had been evaluated at KSC on other occasions.

The laboratory corrosion testing was performed by immersion of two sets of samples in an aerated 3.5 % NaCl aqueous or 0.1 M HCl solution and monitoring the change in the sample's appearance over time. The testing at the Beach Testing Facility at Kennedy Space Center consisted of exposure to severe environmental conditions. The KSC Beach Corrosion Test Site is located on the Atlantic Ocean approximately one mile south of Launch Complex 39A at KSC. The test site is approximately 100 feet from the mean high tide line, with the orientation of the samples facing east toward the ocean at a 45 degree angle, to receive the full extent of sun, rain, and sea spray. The beach exposure test procedure is based on the test method described in ASTM G50[6]. Inspection procedure included visual characterization of the samples for corrosion.

RESULTS AND DISCUSSION

Polyaniline was synthesized chemically according to published procedures.[4] The emeraldine base of polyaniline can be readily dissolved in NMP for coating mild steel substrates. The polymer /NMP solutions were applied to the substrates and doped by immersion in a THF solution containing dopant. The samples were then topcoated with a durable polymer coating for additional abrasion resistance. To establish a baseline of corrosion resistance of the polyaniline coated samples, a set of control samples were prepared with only the topcoat. A portion of both

control samples and those with the primer were scratched with a scribe to expose bare metal. These were tested in the laboratory tests.

The laboratory testing of the polymer coated cold rolled steel coupons (1 X 3/4") was performed in two different solutions via gas/liquid cells. One environment consisted of placing each coupon in an individual vial containing sufficient 3.5 % NaCl solution to cover the coupon. All vials were capped with a rubber septum into which air was bubbled to ensure oxygenation of the solution. In a second environment, a 0.1 M HCl solution was used in place of a saline solution. Photographs were taken of the samples before exposure to the above environments as well as at two to four week intervals throughout the testing period.

The samples coated with the polyaniline primer showed much better corrosion resistance in both environments than those coated with epoxy alone. In fact even when the coatings are scratched to expose bare metal, the polyaniline coated sample show no sign of corrosion. In Figure 1 (left side) is a picture of a steel sample coated with only a clear epoxy topcoat and exposed to 0.1 M HCl for 8 weeks. Signs of corrosion in the scratch and throughout the sample are evident. In Figure 1 (right side) is a steel sample coated with the intensely colored, polyaniline and doped with TCNE

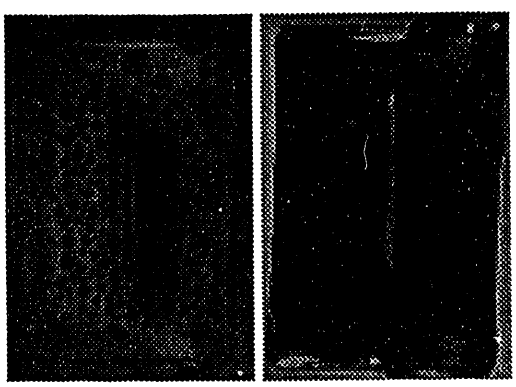

Figure 1.Mild steel samples coated with clear epoxy alone, on the left, and coated with intensely colored TCNE doped polyaniline primer in addition to the clear topcoat, on the right, were scratched with a scribe, exposing bare metal. Each sample was exposed to an aerated solution of 0.1 M HCl for eight weeks.

in addition to the epoxy topcoat and exposed to the same solution for 8 weeks. In contrast to the sample with no primer, this sample shows no sign of corrosion on the edges or in the scratched area. It looks virtually unchanged from when it was placed in the acidic solution.

The testing at the KSC Beach Corrosion Test Site was performed on mild steel samples (4 X 6") exposed to harsh environmental conditions. In addition to its close proximity to salt spray from the

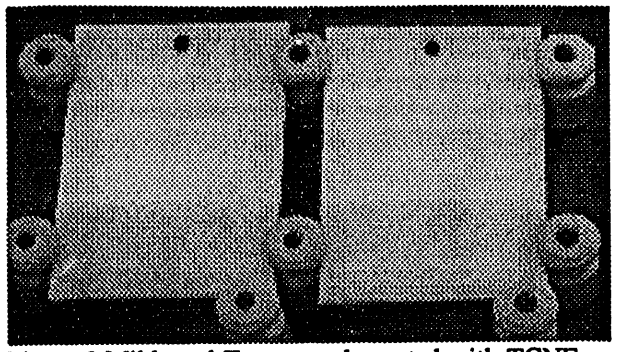

Figure 2.Mild steel Tator panels coated with TCNE or p-toluenesulfonic acid doped polyaniline primer with a polyurethane topcoat were exposed to the environmental testing at Kennedy Space Center for seven months.

ocean, there were several space shuttle launches during its seven month exposure time exposing it to corrosive exhaust gases. Twelve polyaniline samples doped with either TCNE or p-toluenesulfonic acid were topcoated with the polyurethane coating and mounted on a rack at the test site along side two samples with only the polyurethane topcoat. After seven months of exposure there was a noticeable difference between the samples with and without the polyaniline primer coating. A test sample with the

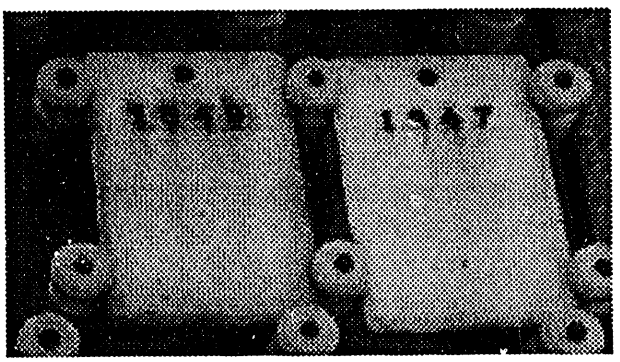

Figure 3.Mild steel Tator panels coated with only a polyurethane topcoat were exposed to environmental testing at Kennedy Space Center for seven months.

polyaniline primer coating shown in Figure 2 looks unchanged from its appearance before testing. In contrast, the sample with the topcoat alone shows signs of corrosion with rust on the edges and in the stamped number area of the sample in Figure 3. These results continue to be evident to date as shown in the sixteen month photographs in Figure 4. There is still a significant improvement in the performance of the polyaniline undercoated samples over those with the topcoat alone.

CONCLUSIONS

The results of our testing indicates that the use of polyaniline as a corrosion resistant primer has great promise. This coating system performs much

better than either the epoxy or polyurethane topcoat alone. Further testing at the KSC Beach Corrosion Test Site is underway to compare the conducting polymer primer with other good performing primers under harsh test conditions. Other testing of

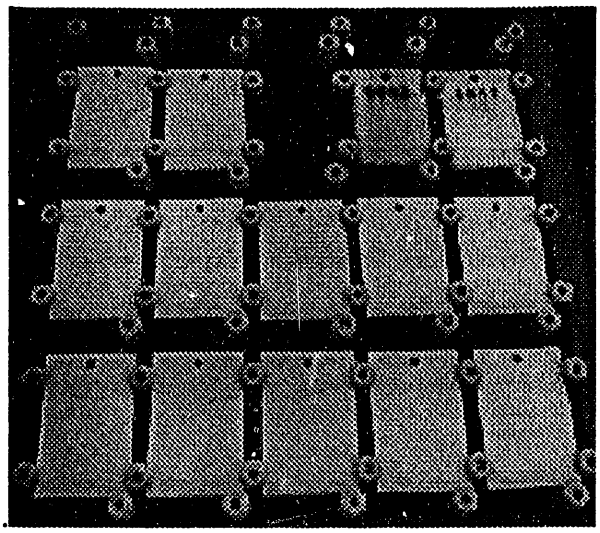

Figure 4.Test samples on the test rack at the Kennedy Space Center Beach Test Site after 16 months of environmental exposure. The samples without the PAn primer coat are located in the upper right hand corner and show signs of rust in stamped numbers.

conducting polymer coated 2025 aluminum test panels is soon to be underway at Kennedy Space Center.

ACKNOWLEDGMENT

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