

Novel Surface Treatment Processes to Protect Metal Substrates

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Introduction

Zinc and its alloys are more electronegative than steel and offer excellent sacrificial protection to underlying steel in corroding media. However, due to the very high electronegativity of these deposits, the rate of dissolution is very high. Chromate conversion coatings have been used extensively to prevent rapid Zn dissolution in aerospace, food processing and automobile industries. Chromium is favored due to its barrier and corrosion resistance properties. Chromium deposition is obtained from hexavalent Cr salt baths, which are subject to stringent regulations. Due to the toxicity of the metal and its salts, use of alternate baths is also undesirable. Effluent treatment in general is a considerable problem. Hence, there exists a need to develop an environmentally friendly coating that is also capable of preventing Zn dissolution. Several studies have been reported for developing chromium-free alternatives. However, these coatings suffer from poor stability and/or high cost.

Elisha Technologies Co., L.L.C. has discovered ways to grow high performance thin silicate based minerals on metallic substrates at low temperatures and ambient pressures.¹ The mineralization process is done using a bath which has no pollutants. Deposition of silica films has been accomplished previously either by sol-gel deposition² or through anodic deposition³ at high voltages. Cheng *et al.*² report the development of an aluminosilicate coating through a sol-gel process in an autoclave at 175°C. While the deposit yields superior corrosion characteristics as compared to Cr conversion coatings, the entire synthesis procedure is laborious, time consuming and is not suited for commercial applications. Speers and Cahoon³ report the deposition of Si from alkaline silicate electrolytes by anodizing of Al at 350 V. However, this process is limited to Al (or similar metals which have stable anodic oxide films) and also involves application of large potentials. Elisha's process is general in nature and can be applied for a wide range of metals. Further, it is inexpensive and the entire process is environmentally friendly. In this paper we report on the development of an electrocatalytic process to grow silica films on zinc substrates. The corrosion characteristics of the deposit have also been studied as a function of bath parameters. The bath properties have been optimized based on the corrosion data obtained. Finally, the mechanism of silica formation will also be presented. The uniqueness of this process is that it can be applied to any metal substrate.

Experimental

The deposition was carried out in a plating cell made of glass with Pt-Niobium anodes. Zinc plated steel panels received from Elisha were used as the cathode. Prior to deposition the panels were degreased with acetone and washed with demineralized water. In the first part of the studies the deposition was done in panels of total surface area 29.1 cm² (anode:cathode ratio = 8:1). Subsequent to optimizing the deposition parameters on the smaller panels, the deposition was carried out in larger galvanized

panels. Zinc plated steel panels (6 in. X 3 in.) of surface area 18 in.² (116 cm²) each side as received from Elisha were used as the cathode. Two different sets of studies were done: (i) First, the effect of applied potential was studied at 75°C at 10 V and 12 V and (ii) Next, the effect of temperature was studied at 70°C, 75°C and 80°C at applied voltages of 10 V and 12 V. For both studies, the deposition time was held constant at 15 minutes. In the next stage, deposition was done in Elisha's bath along with various additives. Similar sets of studies were also done in an Electroless Bath. Subsequent to coating, the panels were removed from the bath and washed with deionized (DI) water. After deposition, one set of samples was rinsed immediately. The second set of samples was left dry and was not washed.

Corrosion Testing

Next, the corrosion characteristics of the panel were studied in 0.01 M Na₂SO₄ solution at pH 6.5. Initial studies conducted in 3.5% NaCl revealed that this represented an aggressive corrosion medium for the panel. Hence, the studies were done in sodium sulfate solutions. A representative panel area of 1 cm² was chosen for testing. The rest of the panel was masked with an insulating tape. A three-electrode setup was used to study the corrosion behavior of the mineralized samples. The electrolyte used in this study is 0.01M (pH =6) and 0.5 M (pH=4) sodium sulfate. Ti coated with Pd was used as the counter electrode. Hg/Hg₂SO₄ was used as the reference electrode. All potentials in this study are referred with respect to the Hg/Hg₂SO₄ electrode. Corrosion studies were done using Scribner Associates Corware Software with EG&G Princeton applied Model 273 potentiostat/galvanostat and a Solartron 1255 frequency analyzer. The electrode was left on open circuit till it's potential stabilized. After the potential stabilized, non-destructive evaluation of the surface was done using linear polarization and impedance analysis.

Separately, samples were prepared for SEM and EDAX analysis. Surface images of bare and mineralized galvanized panels were obtained with a Hitachi S-2500 Delta SEM. Constitutive elements on the surface of the panels were analyzed using energy dispersive analysis with X-rays (EDAX). Electron probe microanalysis (EPMA) was done to map the various elements on the surface of the mineralized sample.

Results from the above studies will be presented and discussed in the presentation. A simple mathematical model will be presented which will explain the processes occurring at the interface during SiO₂ polymerization (adsorption -precipitation).

References

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