# Novel Non Chrome Process for the Protection of Zinc Coatings

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A novel electroless process for depositing corrosion resistant silica layers on metal substrates has been developed. The silicate is deposited from N sodium silicate solution (3.22 weight ratio sodium silicate, 37.5 % solution in water from PQ corporation) in the presence of sodium borohydride. ESCA (electron spectroscopy for chemical analysis) studies of the coating reveal the formation of a very thin (5 nm) zincdisilicate followed by a much thicker (500 nm) silicondioxide layer. An adsorption-condensation mechanism is proposed to account for the two layer silicate formation. Based on this mechanism, the deposition parameters such as the concentration of the PQ bath, the concentration of the reducing agent and the temperature of the operating bath were optimized. Accelerated corrosion tests show a higher barrier resistance and better stability when compared to chrome passivates. The improved corrosion performance of the silicate coatings by the electroless process shows promise as an alternative to conventional hexavalent chrome passivation.

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### Introduction

Phosphate and chromate based conversion coating treatments are widely used to decrease the dissolution of sacrificial coatings [1-3]. Among them, chrome passivates are widely preferred due to their high corrosion resistance, barrier and self-healing properties and the ease with which it is applied. But chrome passivates are generally prepared from hexavalent chromium based baths, which is known for its toxicity [4]. Hence search for alternative corrosion resistant coatings is of interest for researchers. Soluble silicates are economical and environmentally friendly chemicals that have been in use for several decades to protect metals from the corrosive effects of water [5]. They are found to deposit a thin protective film on various metal surfaces. Once the silicate addition in water is ceased, the silica film gets washed away and the corrosion rate increases. Similarly, a thin insulating film of silica was observed when steel was quenched in silica solution [6]. Corrosion resistant coating of colloidal silica along with hexavalent and trivalent chromium was developed as early as 1972 [7]. However the formation of silica coatings for the corrosion protection of steel remains a challenge and is being actively investigated. Cheng *et al.*, [8] developed an aluminosilicate coating through a sol gel process. Jesinowski [9] prepared colloidal silica by precipitation of silicate solution using sulphuric acid in emulsion medium. Recently, Chigane et al., [10] prepared thin films of silica from aqueous fluoride electrolytes by electrolysis. However all these processes are not suited for commercial applications due to either their time intensive nature or the poor quality of silica films formed.

In our earlier work, Veraraghavan *et al.* [11] optimized the operating conditions for the electrolytic process by which silica can be electrodeposited at the cathode. It was found that corrosion resistant silica films can be deposited by electrolyzing in a 1:3 PQ solution (one part of PQ solution dissolved in three parts of water) at 75 °C for 15 mins at an applied potential of 12 V. An inclusion of the post-heating step at 175 °C for 1 hour increases the corrosion resistance and performance of the coatings. It has been shown that hydrogen evolution at the interface helps in the deposition process.

In the present paper we have tried to replicate the electrolytic process by a novel electroless process. The goal was to apply silica films uniformly to any configuration of substrate. Further, the electrolytic process is energy intensive in nature due to application of 12 V during electrolysis and also due to post heating at 175 °C. To make the process less energy intensive, we have developed a novel electroless process by which silica films can be deposited on zinc substrates. The naturally available hemimorphite form of zinc disilicate has been reproduced by this process.

### Experimental

Silica depositions were performed on zinc plated steel panels (EZG-60G) of surface area 116 cm<sup>2</sup> each side, as obtained from ACT labs. Zinc was coated on the steel substrate using electrodeposition at a current density of 30 mA/cm<sup>2</sup> at room temperature from an acidic (pH 4.0) bath containing 300 g/L ZnSO<sub>4</sub>, 30 g/L ZnCl<sub>2</sub> and 30 g/L H<sub>3</sub>BO<sub>3</sub>. The thickness of the coating is 13  $\mu$ m. Prior to silica deposition, the samples were degreased with acetone and washed with demineralized water. The N Sodium silicate solution (PQ corporation, 37.5 wt% silicic acid, sodium salt in 62.5 wt% water) with a SiO<sub>2</sub>:Na<sub>2</sub>O ratio of 3.22 was used as a silicate precursor.

The depositions were carried out in 2 litre plating cell made out of glass. Common reducing agents used in literature are sodium hypophosphite, sodium borohydride and hydrazine. Among these the last one hydrazine is highly toxic and is not desirable for use while developing an environmentally friendly process. Sodium hypophosphite precipitates in PQ solution and leads to instability of the bath. Sodium borohydride exhibits none of these characteristics and has been explored in detail for getting better deposits. The experimental study consisted of optimizing the concentration of the PQ bath, amount of NaBH<sub>4</sub> used and analyzing the mechanism of deposition.

The corrosion characteristics of all the panels were tested in 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution at pH 4.0. A three-electrode setup was used to study the corrosion behavior of the mineralized samples. The panel under study served as the working electrode, Pt was used as the counter electrode and SCE (Standard calomel electrode) was the reference. Once its potential stabilized after immersion in solution, Non-destructive evaluation of the panel surface was done using linear polarization. During linear polarization, the potential was varied 10 mV above and below the open circuit potential at a scan rate of 0.1667 mV/s. All measurements were performed with an EG & G PAR model 273A potentiostat interfaced with a computer. The same was repeated in three different spots to check the uniformity. Accelerated corrosion testing was carried out using an Atotech environmental test chamber model P22E001. The samples were exposed to a constant 5 % salt fog in accordance with the ASTM B-117 specifications. The appearance of the white rust, red rust and the failure of the samples were observed as a function of time in hours. Five percent of red rust on the surface of the samples was the basis for the failure criterion.

Surface morphology of the coatings was analyzed by viewing them under a Hitachi S-2500 Delta scanning electron microscope (SEM). Constitutive elements on the surface of the panels were analyzed using energy dispersive analysis with X-rays. XPS (X-ray photoelectron spectroscopy) analysis was used to estimate the nature of the coating. XPS results were obtained using a Hewlett-Packard 5950 A XPS spectrometer that is capable of generating monochromator X-rays at a background pressure of 5 X  $10^{-9}$  Torr. After calibration, the depth profile of the coating was analyzed by sputtering it with the X-ray and the structure of the coating was determined. This procedure has been described in detail elsewhere [12] and is used in many silicate related fields.

#### **Results and Discussion**

Initially, silica is deposited from diluted PQ solution by the electroless process. The electrolyte used for the deposition of silica is a 3.22 N PQ solution diluted 8 times in water with 5 g/L of NaBH<sub>4</sub>. Deposition was done at 75 °C for 15 minutes. Subsequent to deposition, the samples were left to dry in air for 24 hrs and then rinsed. Silica content detected on the surface was found to be around 13.7 wt %, the rest being zinc. Linear polarization studies in a 0.5 M Na<sub>2</sub>SO<sub>4</sub> (pH 4.0) solution were performed on several spots of the silicated sample to estimate the average corrosion resistance. The average corrosion resistance of the sample was 1432 Ohm-cm<sup>2</sup>. The obtained corrosion resistance is comparable to that of the silica deposit by electrolytic



Figure 1: Comparison of the EDAX spectrum for (a) bare galvanized steel and (b) galvanized steel coated with silicondioxide.



Figure 2: Cross section view of the  $SiO_2$  coating prepared by electroless process on a galvanized steel sample (Magnification at 90.0 k).

process [11]. It is also greater than the resistance of commercial available passivates like yellow chrome (1367 Ohm-cm<sup>2</sup>). Bare Zn has a low resistance of 286 Ohm-cm<sup>2</sup> and coating it with silica by the electroless process results in an increase of nearly five times in corrosion resistance. Figure 1 shows the EDAX analysis of a sample silicated by the electroless process. Also shown is the EDAX spectrum for bare zinc sample.

The thickness of the coating was evaluated with a cross sectional image at high magnification. Figure 2 show the cross sectional picture of the electrogalvanized zinc panel

prepared by the electroless process. The thickness of the silica layer deposited is around 500 - 600 nm. Also, the cross section reveals the presence of two distinct layers, a thin layer immediately over metallic zinc followed by a thick layer. Further, studies were performed to analyze the nature of the coatings and mechanism of deposition.

#### XPS Results and Mechanism of Silica Deposition:

To analyze the nature of the coating, characterization was carried out using X-ray photoelectron spectroscopy (XPS). The surfaces were characterized using a variety of XPS peak positions [14]. The resulting binding energy (B.E) for the Si 2p peak was the main basis for our study. From the XPS analysis, the observed binding energy of Si (2p) varied with sputtering indicating the presence of different layers. For the first layer over metallic zinc, the observed binding energy was close to 102.2 eV, and this corresponds to Si found exclusively in the disilicate form. Based on this, it is observed that the first layer corresponds to that of zinc disilicate (Zn<sub>4</sub>Si<sub>2</sub>O<sub>7</sub>(OH)<sub>2</sub>.H<sub>2</sub>O) and the depth of the layer is around 5 nm. However, the naturally occurring zinc disilicate, namely the hemimorphite form has a binding energy of 101.8 eV. The 102.2 eV B.E can be considered as disilicate species owing to the trend of the Si 2p shifts found for polymerized species [12-14]. As we move from monomeric to polymeric species, the covalency of the Si-O bonds decreases and the Si 2p binding energy increases. This leads to an increase in the binding energy of the Si 2p close to 102.2 eV.

The formation of this zinc disilicate can be explained based on a simple adsorption process.  $SiO_2$  dissolves in water to form monomeric  $Si(OH)_4$  species. It is widely called as silicic acid. The amount of the  $SiO_2$  hydrolyzed to  $Si(OH)_4$  is dependent on the pH and temperature of the silicate solution. In general equilibrium exists between  $SiO_2$  and silica monomer according to the equation.

$$SiO_2 + 2 H_2O = Si(OH)_4$$
 [1]

According to Iler [16], the monomeric species  $Si(OH)_4$  condenses with any preexisting solid surface that bears OH groups with which it can react, namely SiOH, or any MOH surface, where M is a metal that will form a silicate at the pH involved. In the present case, the Zn substrate is immersed in alkaline sodium silicate solution with a pH around 11.0. Pourbaix diagrams show that zinc dissolves at such alkaline pH and Zn cannot exist as  $Zn^{2+}$ . They will be present as zincate and/or bizincate ions. The surface of the Zn substrate is now covered with a thin layer of Zn hydroxide (Zn(OH)<sub>2</sub>). The monomeric Si(OH)<sub>4</sub> species reacts with the receptive surface to form zinc silicate by the following reaction:



Hence, the thin layer of zinc disilicate (Zn<sub>4</sub>Si<sub>2</sub>O<sub>7</sub>(OH)<sub>2</sub>.H<sub>2</sub>O) is formed by the adsorption process as mentioned above and proceeds through out the receptive surfaces available.

For the second layer, the B.E energy of Si (2p) shifts to greater values of 103.3 eV and O(1s) to 532.7 eV indicating the presence of SiO<sub>2</sub>. The coating status remains the same to a depth in excess of 500 nm, suggesting an SiO<sub>2</sub> layer of 500 nm in thickness. Above this silica layer, trace amounts of carbonaceous systems like sodium carbonate (BE. 287 eV) and Na<sub>2</sub>SiO<sub>4</sub> were also observed and they correspond to the impurities adhering on the surface. Once the receptive surface is covered by zinc disilicate, further growth of the silica is the molecular deposition of SiO<sub>2</sub>.

The mechanism for the molecular deposition of  $SiO_2$  from  $Si(OH)_4$  is a condensation reaction catalyzed by the presence of OH groups, presence of salts, rate of dehydration and operating temperature. In the present case the pH of the operating bath is 11.0 and hence condensation of the monomeric silica is catalyzed. The deposition of  $SiO_2$  is indeed the reverse of the dissolution of silica as shown in equation 1. In the condensation reaction, two silanol groups of the silicic acid condense to form a siloxane groups with the removal of water as follows:

$$- \begin{array}{c} | \\ \text{Si} - \text{OH} + - \begin{array}{c} | \\ \text{Si} - \text{OH} \end{array} \rightarrow - \begin{array}{c} | \\ \text{Si} - \text{O} \end{array} - \begin{array}{c} | \\ \text{Si} - \text{O} \end{array} \rightarrow \begin{array}{c} | \end{array} \rightarrow \begin{array}{c} | \\ \text{Si} - \text{O} \end{array} \rightarrow \begin{array}{c} | \end{array} \rightarrow$$

The removal of water or the dehydration process catalyzes this reaction. Significantly, in the electroless process, reducing agent sodium borohydride helps in dehydration at the interface of the electrolyte and substrate. Removal of the water at the interface takes place through the following reaction.

$$NaBH_4 \rightarrow Na^+ + BH_4^-$$
  
BH<sub>4</sub><sup>-</sup> + 2 H<sub>2</sub>O  $\rightarrow$  4 H<sub>2</sub> + BO<sub>2</sub><sup>-</sup>  
BO<sub>2</sub><sup>-</sup> + Na<sup>+</sup>  $\rightarrow$  NaBO<sub>2</sub> [4]

Also the operating temperature of 75 °C increases both the dehydration process and the kinetics of sodium borohydride decomposition (equation 4). Condensation proceeds till a predominant amount of silanol groups present are used up for the production of siloxane bonds. Thus the silicate formation is by an adsorption – condensation mechanism, which proceeds in two stages namely, (i) formation of zinc disilicate by an adsorption process and (ii) condensation of the silicondioxide over zinc disilicate. As seen from the mechanism, the formation of the silicate coatings is strongly dependent on the operating temperature, concentration of monomeric species and rate of dehydration. The next set of studies is aimed at increasing the silica content in the deposit by optimizing the above parameters.

### Effect of Bath Temperature:

Increase in bath temperature increases the rate of sodium borate formation (equation 4). Also according to Iler [16],  $SiO_2$  formation is favored in hot solutions. Samples were prepared in 1:8 PQ solution with 5 g/L of NaBH<sub>4</sub>. Deposits prepared at room temperature had a very low

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[3]

amount of silica content (less than one weight percent). With increase in bath temperature silica content increases and an optimum amount of silica of nearly 13.7 wt % was observed when deposited at a bath temperature of 75 °C. With further increase in bath temperature, no significant increase in silica content was observed. To determine the effect of bath temperature, corrosion characteristics of the coatings were determined by linear polarization. The corrosion resistance for the deposit prepared at room temperature was 300 Ohm-cm<sup>2</sup>, which is similar to that of a bare galvanized steel sample. Deposits prepared at 75 °C show resistance value close to 1400 Ohm-cm<sup>2</sup>. Hence the operating bath temperature for the electroless process was fixed at 75 °C.



Ratio of PQ Bath

Figure 3: Average corrosion resistance and silica weight percent of deposits as a function of the concentration of PQ bath. Concentration is expressed as a ratio between volume of PQ solution and water.

#### *Effect of PQ Concentration:*

Altering the concentration of the PQ solution can vary the silica content in the deposit. To study this, depositions were carried out in 1:8, 1:5, 1:3 and 1:1 (v/v) mix of PQ : water. Depositions were performed for 15 minutes in the presence of 5 g/L of NaBH<sub>4</sub>. Figure 3 summarizes the average corrosion resistance and silica content of the samples as a function of the concentration of the PQ solution. From the plot, it is evident that the corrosion resistance and silica weight percent increases with increase in concentration of the PQ solution. The increase in concentration of the monomeric species increases with increase in concentration of PQ solution favoring silica formation. Beyond 1:3 PQ, not much increase in the corrosion resistance and silica weight percent was observed. Thus 1:3 PQ bath was chosen to be the optimum PQ concentration to be used in the electroless process.

#### Effect of Sodium Borohydride:

The effect of sodium borohydride concentration was studied in the 1:3 PQ bath. Depositions were carried out on galvanized steel panels at 75 °C for 15 mins in the presence of sodium borohydride. The borohydride concentration was varied from 3 g/L to 9 g/L. The deposited samples were dried in air for 24 hrs and rinsed in water. To add emphasis on the role of sodium borohydride, samples prepared in the absence of sodium borohydride were also tested and compared. The amount of sodium borohydride was optimized based on the corrosion performance of the coatings. The deposits prepared with various concentrations of borohydride



*Figure 4: Silica content as a function of sodium borohydride concentration.* 

 Table I. Comparison of resistances of deposits prepared by electroless process with different concentration of sodium borohydride

Time	Average Corrosion Resistance (Ohm-cm <sup>2</sup> )			
(No of days)	0 g/L	3 g/L	6 g/L	9 g/L
Initial	1323	1870.1	1941.5	2168.9
1 <sup>st</sup> day	632.1	1650.7	1660.2	2071.7
4 <sup>th</sup> day	601.1	1072.1	1491.8	1856.2
7 <sup>th</sup> day	560	830.1	1372.1	1590.1

were left immersed in water for a span of one week and the silica content were analyzed by EDAX analysis initially and after immersion for one week. The average corrosion resistance was measured in a 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution, pH 4.0 at regular intervals. Table I represents the corrosion resistance of the deposits as a function of time. Resistance values show that the corrosion resistance and stability of the coating increases with increase in the concentration of sodium borohydride. Beyond 6 g/L addition, the increase in the corrosion resistance was less pronounced. Samples prepared in the absence of sodium borohydride (0 g/L) have an initial corrosion resistance of 1323 Ohm-cm<sup>2</sup>. This initial resistance value is comparable to that of the chrome passivates, but the stability of the coating in aqueous media is very low. The average corrosion resistance drops to 630 Ohm-cm<sup>2</sup> when exposed in aqueous media for a day. However, samples prepared with 6 g/L of sodium borohydride have a corrosion resistance of 1372 Ohm $cm^2$  even after immersion in water for a week. From the corrosion values it is seen that the stability of the coating in aqueous media increases with sodium borohydride concentration used. The increase can be attributed to the removal of the water at the panel interface due to sodium borohydride decomposition, which enhances the condensation of silica layer, thus forming dense silica films. This is evident from the values of the silica content measured initially and after immersion in water for a week (presented in Figure 4). With the use of 3 g/L of sodium borohydride, the silica weight percent in the deposit increases from 11.75 % (0 g/L of sodium borohydride) to 23.338 %. This increase in the silica content with sodium borohydride adds proof to the mechanism of SiO<sub>2</sub> layer formation as mentioned earlier. Values of silica content after corrosion indicate that the silica content decreases rapidly for the samples prepared in the absence of sodium borohydride. The decrease in the silica content due to corrosion reduces with increase in the sodium borohydride concentration in the bath. Beyond 6 g/L of sodium borohydride, no significant increase in the silica content and corrosion resistance of the deposit is seen. Hence the amount of sodium borohydride is optimized as 6 g/L.

### Performance of coating in comparison with other conversion coatings

To evaluate the performance of the coating in accelerated corrosion conditions, salt spray testing was performed on silica coated panels. Also, samples coated with other commercially available conversion coatings such as phosphating and chrome passivation were tested for comparison. Figure 5 shows the appearance of the various coatings under ASTM B117 test conditions and the results of the corrosion testing are summarized in Figure 6. Five percent surface coverage with red rust was the failure criterion. Galvanized steel sample with out any further passivation or coating failed in just a span of 48 h (not shown in Figure 5). Among the commercially available coatings, passivation with yellow chrome showed better results compared to that of phosphating and clear chrome processes. With yellow Chrome process, red rust appeared at 312 h and the sample failed at 560 h. But on the control panels coated with silica based on electroless process, the red rust appeared after 552 h and the sample failed at 600 h. With the presence of a thin silica layer, the salt spray corrosion time extends to nearly ten times over the untreated galvanized steel panel. A comparison of the corrosion data of the panels shows the superior performance of the silicondioxide based coating prepared by electroless method.





(d)

Figure 5: Appearance of various conversion coatings and in a salt spray chamber. (a) Yellow chrome after 168 hr NST, (b) Zn phosphating at 96 hr, (c) Clear chrome at 96 hr and (d) Electroless SiO<sub>2</sub>at 168 hr



Figure 5: Comparison of corrosion data for different conversion coatings subjected to accelerated corrosion in a salt spray chamber.

### Conclusions

A novel non chrome electroless process for the deposition of silica films has been developed. XPS studies reveal that the coating is composed of two layers, an underlying zincdisilicate layer and a thick silicondioxide layer. A brief mechanism on the formation of two layers has been discussed. The operating parameters for the electroless process such as the concentration of the PQ solution, operating temperature and the amount of reducing agent (sodium borohydride) were optimized based on the corrosion characteristics of the coatings. Samples prepared for 15 minutes from 1:3 PQ solutions at 75 °C with 6 g/L sodium borohydride show the best stability in aqueous media. Comparison of the corrosion data from salt spray chamber show the improved performance of the silicondioxide coating compared to other substrates like cadmium, iron, aluminum etc.

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