NOVEL NON-CHROME PROCESS FOR PROTECTION OF ZINC COATINGS

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A novel process for protection of zinc substrates by silicondioxide has been explored as a promising alternative to the chrome passivation process. The silicate is deposited from 3.22 N PQ solution ($Na_2O:SiO_2$) by a novel electroless method. The coating characteristics were studied using SEM (Scanning Electron Microscopy), EDX (Energy Dispersive Analysis with X-Rays) and XPS tools. 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. ESCA (electron spectroscopy for chemical analysis) analysis of the coating reveals the formation of zincdisilicate and silicondioxide layers. Accelerated corrosion tests show a higher barrier resistance and better stability when compared to chrome passivates.

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INTRODUCTION

Zn, Zn-Ni and cadmium coatings are some of the widely used coatings for the corrosion protection of steel [1-3]. These coatings are generally termed sacrificial coatings for they dissolve preferentially owing to their electronegative rest potential in comparison with steel. Zn is one of the prominent coatings that is widely favored owing to its sacrificial and environmentally benign properties. However the rate of dissolution of zinc coatings are very high due to the wide difference in the potential between the zinc (-1.123 V vs. SCE) and the underlying steel substrate (-0.554 V vs. SCE). In general, Zn is alloyed with nickel, cobalt and iron to decrease the dissolution rate [4-6]. Use of phosphate and chromate based conversion coating treatments is an alternate way to reduce the dissolution of zinc [7-9]. Use of conversion coatings in automobile and aerospace industries are of commercial interest. Chrome passivates are the widely used coatings to reduce the dissolution of zinc [8,9]. They are widely preferred for their high corrosion resistance, barrier and self-healing properties and the ease with which it is applied. But the chrome passivation is generally prepared from hexavalent chromium based baths, which are known for its toxicity [10]. Due to its high toxicity, hexavalent chromium based baths are subject to stringent regulations and the effluent treatment is a costly and time-consuming process. European Union has banned the use of hexavalent chromium by 2006. Trivalent chrome based coatings and phosphating are some of the other common processes prevalent in the industry. Trivalent chrome, though less toxic, is again a chromium based coating and its use is of environmental concerns. Further development of an better environment friendly coating with high corrosion characteristics is of commercial interest.

Soluble silicates are economical and environmentally friendly chemicals that are in use for several decades to protect metals from the corrosive effects of water [11]. They are found to deposit a thin protective film on to various metal surfaces. Once the silicate addition in water is ceased, the silica film gets washed away and corrosion rate increases. Similarly, a thin insulating film of silica was observed when steel was quenched in silica solution [12]. Corrosion resistant coating of colloidal silica along with hexavalent and trivalent chromium was developed as early as 1972 [13]. However the formation of silica coatings for the corrosion protection of steel remains a challenge and is being actively investigated explored. Cheng et al [14] have developed an aluminosilicate coating through a sol gel process. Jesinowski [15] prepared colloidal silica by precipitation of silicate solution using sulphuric acid in emulsion medium. Recently, Chigane et al., prepared thin films of silica from aqueous fluoride electrolytes by electrolysis [16]. However all these processes are time consuming and are not suited for commercial applications.

Elisha Technologies Co., L.L.C. [17] discovered a novel way to grow high performance thin silicate based oxide that mimics the structures of the Si minerals found in nature. The silicate precursor was transformed into the metal surface with the help of organic carriers like polyurethane. The mineral layer, which stays on the surface after the removal of the organic carrier, was found to naturally ‘passivate’ the metallic surfaces. More recently, Elisha has also discovered a novel method to synthesize silicates from sodium silicate solution by electrolysis[18]. 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 our earlier work, Veraraghavan et al [19] optimized the operating conditions for the electrolytic process to improve the performance of the coating. 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 ^{o}C for 15 mins at an applied potential of 12 V. An inclusion of the post-heating step at 175 ^{o}C for 1 hr 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 Elisha mineralization process by a novel electroless process. With our expertise in silica film deposition, we have developed a novel electroless process by which silica films can be deposited on zinc substrates. The same process can also be extended to other substrates like cadmium, iron, aluminum etc.

EXPERIMENTAL

Silica depositions were performed on zinc plated steel panels of dimensions 6 inch X 3 inch obtained from ACT labs. Prior to deposition, the samples were degreased with acetone and washed with de-mineralized water. Sodium silicate solution with a SiO_2:Na_2O ratio of 3.22 [from PQ corporation] was used as a silicate precursor. The depositions were carried out in 2 litre plating cell made out of glass. The experimental study consisted of optimizing the concentration of the PQ bath and amount of $NaBH_4$ used. A detailed study of the corrosion characteristics of the coating was also done. The effect of concentration of the operating bath was studied by varying the concentration of 3.22 N PQ solution in the bath. Studies were performed in 1:8,1:5, 1:3 and 1:1 (v/v) mix solutions of PQ: water. For example, 1 litre of 1:3 PQ bath is prepared by dissolving 250 ml of 3.22 N PQ solution in 750 ml of water. The bath temperature was maintained at 75 ^{o}C and the depositions were carried out for a period of 15 mins. The amount of $NaBH_4$ was varied to optimize its amount to be used in the deposition process. The stability of the coatings was studied by evaluating the corrosion resistance of the coated samples immersed in water over a period of time. Linear polarization studies were done to determine the corrosion resistance of the coatings. The potential was swept linearly from + 10 mV to –10 mV vs. E_{corr} at a scan rate of 0.3 mV/s. Polarization resistance was calculated from the slope of the resulting graph of overpotential vs. current density. Separately, nondestructive testing of the surface was performed on a representative panel area of 1 cm^2 in a 0.5 M Na_2SO_4 solution at pH 4.0. Pt foil was used as counter electrode and standard calomel electrode was used as the reference electrode. All measurements were performed with an EG & G PAR model 273A potentiostat. Results were evaluated using Scribner Associates Corrware Software. 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. While XPS analysis was used to estimate the nature of the coating. ESCA results were obtained using a Hewlett-Packard 5950 A ESCA spectrometer.

RESULTS AND DISCUSSION

During electroplating hydrogen is evolved on the surface of the cathode and the rate of hydrogen evolution can be controlled by varying the applied potential or current. However, in case of electroless deposition this can be accomplished only with the use of selective reducing agents. Common reducing agents used in literature are sodium hypophosphite, sodium borohydride, dimethyl amino borane and hydrazine. Among these the last one hydrazine is highly toxic and cannot be used for our studies. Sodium hypophosphite precipitates in PQ solution and leads to instability of the bath. Dimethyl amino borane is stable in solution but inhibits the precipitation of silicates on the surface of zinc. Sodium borohydride exhibits none of these characteristics and has been explored in detail for getting better deposits.

Silicondioxide 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. The silica is deposited from the 1:8 PQ silicate solution in the presence of 5 g/L of $NaBH_4$ at 75 ^{o}C for 15 minutes. Silica content detected on the surface was found to be around 13.7 wt %, the rest being zinc and impurities. The silicated samples were left to dry in air for 24 hrs and then rinsed. Linear polarization studies in a 0.5 M Na_2SO_4 (pH 4.0) solution were performed on several spots of the silicated sample to estimate the average corrosion resistance. The corrosion resistance of the sample was about 1400 Ohm-cm^2. This value is greater than compared to the commercial available passivates like yellow chrome (800 Ohm-cm^2). Bare Zn has a low resistance of 300 Ohm-cm^2 and the silicate coated samples by electroless process show an increase of nearly five times in corrosion resistance.

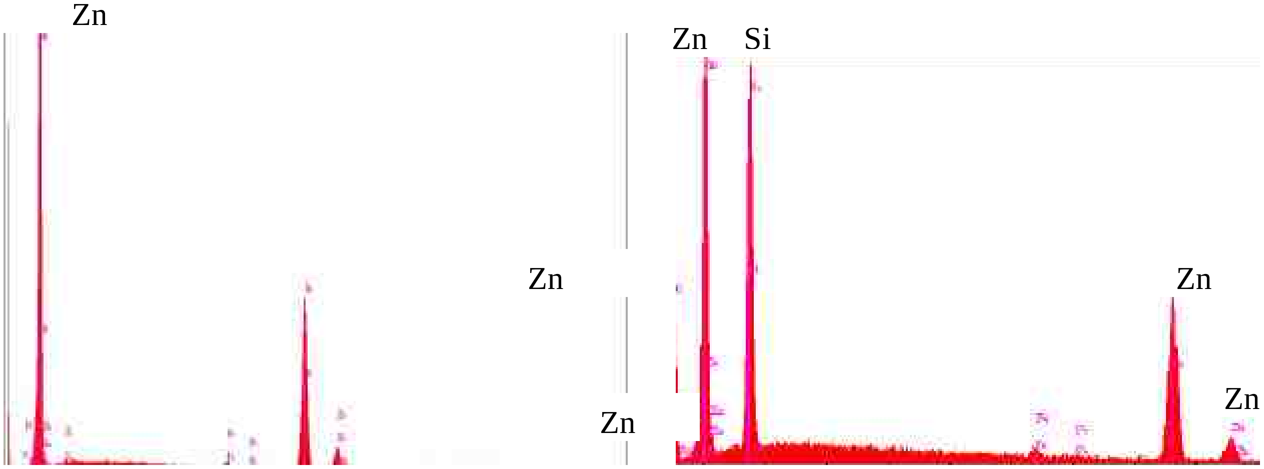


Figure 1. Comparison of the EDAX spectrum for a bare galvanized steel and galvanized steel coated with silicondioxide

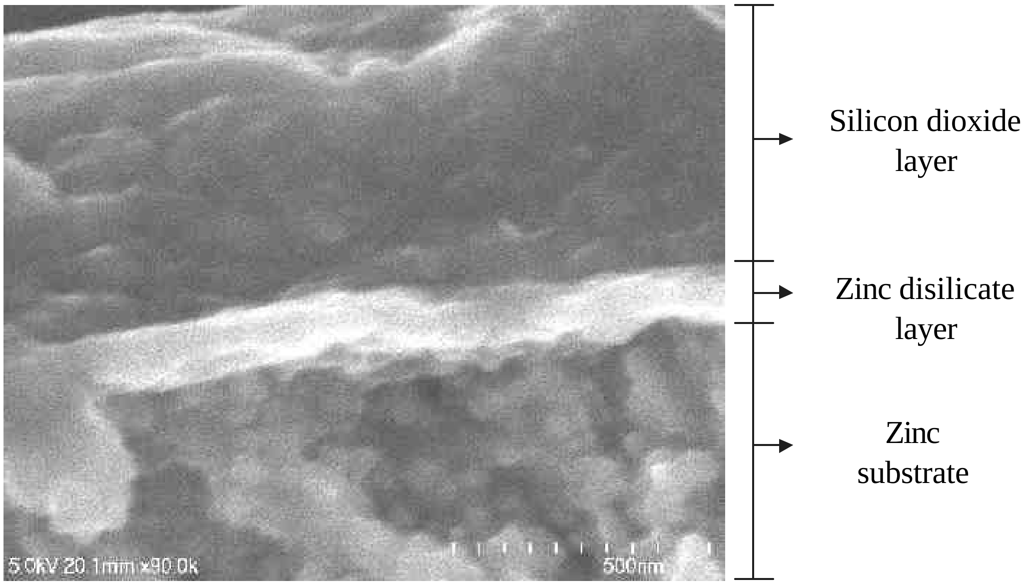


Figure 2: Cross section view of the SiO_2 coating prepared by electroless process on a galvanized steel sample

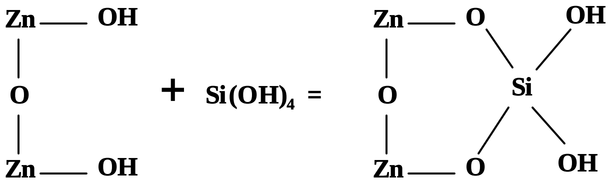
Figure 1 shows the EDAX analysis of a sample silicated by the electroless process. Also shown is the EDAX spectrum for bare zinc sample.

Figure 2 show the cross sectional picture of the electrogalvanized zinc panel prepared by the electroless process. The cross section reveals the presence of two distinct layers, a first layer of thickness 5 nm and a second layer of thickness 500 nm. To analyze the nature of the coating, characterization was carried out using X-ray photoelectron spectroscopy (XPS) also known as electron spectroscopy for chemical analysis (ESCA). The surfaces were characterized using a variety of ESCA peak positions [20]. The resulting binding energy for the Si 2p was the main basis for our study. From the XPS analysis, it is observed that the first layer corresponds to that of zinc disilicate while the second layer corresponds to that of SiO_2. After a removal of 6000 to 7000 A of the coating, underlying metallic zinc is revealed, which essentially suggests a thickness of around 6000 to 7000 A for the silicondioxide coating prepared by electroless process. Initial sputtering reveals the presence of trace of carbonaceous systems like sodium carbonate (BE 287 eV) and later Na_2SiO_4. On further sputtering, BE of Si (2p) rapidly shifts to greater values of 103 eV and O(1s) to 532.7 eV indicating the presence of SiO_2. The coating status remains the same to a depth in excess of 5000 A, suggesting an SiO_2 layer of 5000 A in thickness. Further sputtering shifts the binding energy of Si (2p) close to 102.2 eV. The resulting binding energies of these silicates are found to be exclusively of the disilicate form, i.e hemimorphite. The depth of the zinc disilicate layer was around 50 A. Sputtering beyond this shows metallic zinc.

Thus the silica deposition is expected to take place by a two step process. The first step is the formation of zinc silicate and the second being the precipitation of the silicondioxide layer. The formation of Zinc silicate is 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

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

According to Iler [21], 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 a the pH involved. In the present case, the Zn substrate is immersed in a pH of alkaline sodium silicate solution of pH around 10.5. Pourbaix diagrams show that zinc dissolves at such alkaline pH and Zn cannot exist as Zn^{2+}. They will be present as bizincate ions. The surface of the Zn substrate is now filled with a thin layer of Zn hydroxide ($Zn(OH)_2$). The monomeric $Si(OH)_4$ species reacts with the receptive surface to form zinc silicate by the following reaction.



[2]

Once the receptive surface is covered by the above reaction, further deposition is silica on silica, thus building up a thick film.

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. Significantly, the reducing agent sodium borohydride used helps in dehydration at the interface of the electrolyte and substrate. Removal of the water at the interface takes place through the following reaction.

$NaBH_4 \rightarrow Na^+ + BH_4^-$ [3]

$BH_4^- + 2\,H_2O \rightarrow 4\,H_2 + BO_2^-$ [4]

$BO_2^- + Na^+ \rightarrow NaBO_2$ [5]

Also the operating temperature of 75 °C increases dehydration and kinetics of sodium borohydride reaction. Thus a second layer of condensed SiO_2 over zinc silicate is expected to form. However, the formation of the second layer by condensation is still not clear and a detailed study to understand the exact mechanism is in progress. As seen from the mechanism, the formation of the silicate coatings is strongly dependent on the concentration of monomeric species and rate of dehydration. The next set of studies is aimed at increasing the silica content in the deposit.

Operating temperature of the bath is one of the significant factor that determines the silicate formation by electroless process. Increase in bath temperature increases the rate if the sodium borohydride reaction (equation 3). Also according to Iler [21], SiO_2 formation is favored in hot solutions. Samples were silicated from 1:8 PQ solution in the presence of 5 g/L of $NaBH_4$. Deposits prepared at room temperature had a very low amount of silica content, less than one percent. With increase in bath temperature silica content increases and an optimum amount of silica of nearly 13.7 % 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 polarization resistance for the deposit prepared at room temperature was as low as 300 Ohm-cm^2, which is the very close to that of a bare galvanized steel sample with out any coating. Deposit prepared at 75 °C show resistance value close to 1200 Ohm-cm^2. Hence the operating bath temperature for the electroless process was fixed at 75 °C.

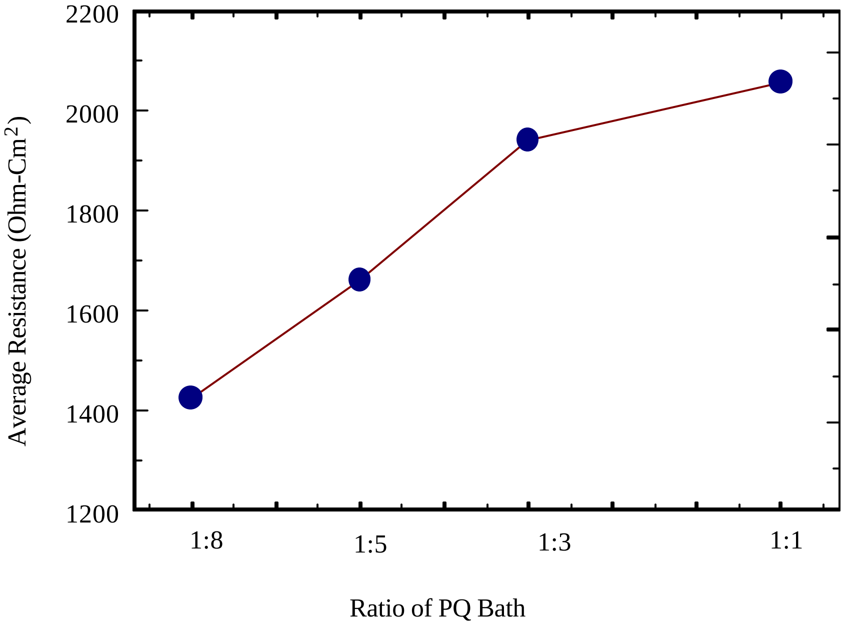


Figure 3: Average corrosion resistance of deposits as a function of the concentration of PQ :water bath

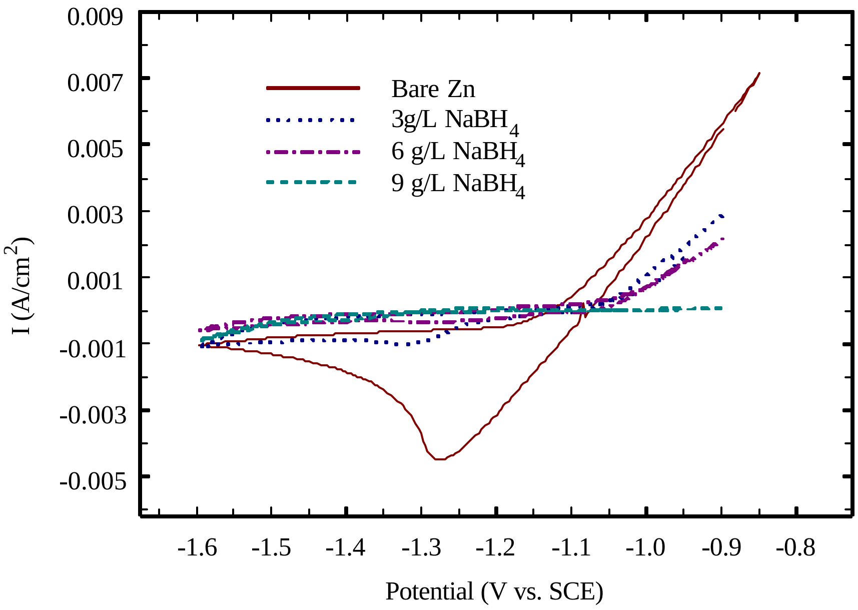


Figure 4: Cyclic voltammograms for deposits obtained at different concentrations of sodium borohydride. CVs were obtained in a 0.5 M Na_2SO_4 solution, pH 4.0.

Altering the concentration of the PQ solution can vary the silica content in the deposit. To study the effect of concentration of PQ solution, depositions were carried out in different concentration of PQ solution in water. The concentrations being 1:8, 1:5, 1:3 and 1:1 (v/v) mix of PQ : water. Depositions was performed for 15 minutes in the presence of 5 g/L of $NaBH_4$. The concentration of the PQ bath was optimized by performing the corrosion tests on the coatings. Figure 3 summarizes the average corrosion resistance of the samples as a function of the concentration of the PQ solution. The corrosion data are the polarization resistance of the coating measured by linear polarization technique in a 0.5 M Na_2SO_4 , pH 4.0 solution . From the resistance values, it is evident that the polarization resistance increases with increase in the concentration of the PQ solution. Beyond 1:3 PQ, higher concentrations are not favored owing to the increased viscosity of the operating bath and the feasibility of an industrial process. Thus 1:3 PQ bath was chosen to be the optimum PQ concentration to be used for the electroless process.

It is essential to optimize the amount of sodium borohydride to be used in the electroless process. The optimized bath concentration of 1:3 PQ was maintained to determine the effect of sodium borohydride concentration. Depositions were carried out on galvanized steel panels from a bath of 1:3 PQ solution at 75 ^oC 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 analyze the effect of sodium borohydride, initially the coverage of the surface by these silicate coatings is estimated with the help of cyclic voltammetry.

Cyclic voltammetry studies were done in a three-electrode setup using a calomel reference electrode in 0.5 M Na_2SO_4, pH = 4.0. Voltammograms were obtained by recording the current while varying the applied potential from –1.6 V to –0.8 V and back to –1.6 V at a scan rate of 5 mV/s. Figure 4 presents the CVs obtained for samples prepared with different amounts of $NaBH_4$ and then left to dry in air for 24 hours. The CV obtained from the Bare Zn galvanized sample has been shown for comparison. The currents on shifting the potential from –1.6 V to more positive values than –1.1 V correspond to corrosion of the surface layer. Increasing the potentials to values more positive than –1.1 V leads to stripping of Zn from the substrate. In the reverse scan Zn deposition happens and a peak appears in the current corresponding to the mass transfer limited current. Similar results are seen for all samples. However, the peak reduction current and the maximum in the oxidation current decrease rapidly with the SiO_2-coated samples. This massive decrease in the current for a bare Zn sample and a Zn sample coated with silicondioxide represents the ability of the coatings to inhibit the corrosion process. Since, the currents are dependent on the amount of material lost from the surface the CVs can be used to obtain a rough estimate of the inhibiting efficiency of silica on Zn. The inhibiting efficiency can be obtained from the following expression:

$$\text{InhibitingEfficiency}(\%)=1-\frac{\text{PeakCurrentinElishasample}}{\text{PeakCurrentinBaresample}}\text{X100}$$

Figure 5 shows the inhibiting efficiency of the samples mentioned above. We can see that increasing the amount of $NaBH_4$ helps in increasing the inhibiting efficiency. Corrosion processes are inhibited to a greater extent with the silicate coating. Also the increase in the concentration of the sodium borohydride decreases the corrosion process further. To analyze the corrosion behavior, the samples were immersed in water over a span of one week and the cyclic voltammetric studies were performed in 0.5 M Na_2SO_4, pH = 4.0 in the same potential window and the inhibiting efficiencies were calculated. The inhibiting efficiency was as high as 70 % .The inhibiting efficiency dropped only by 10 % even after immersion in a corrosive media over a span of week. Figure 6 shows the effect of sodium borohydride on the amount of silica deposited in the galvanized sample. It can be observed that the silica content increases with increase in the concentration of sodium borohydride used in the deposition bath. The increase in concentration of the sodium borohydride helps in increasing the silica content in the deposit. Veeraraghavan et.al. [19] have reported that, the corrosion properties are dependent on the amount of silica content and the corrosion resistance of the coating increases with increase in the silica weight percent in the deposit. To optimize the amount of sodium borohydride, the corrosion performance of the coatings are analyzed. The deposits prepared with various concentrations of borohydride were left immersed in water solution for a span of one week and the silica content were analyzed by EDAX analysis.

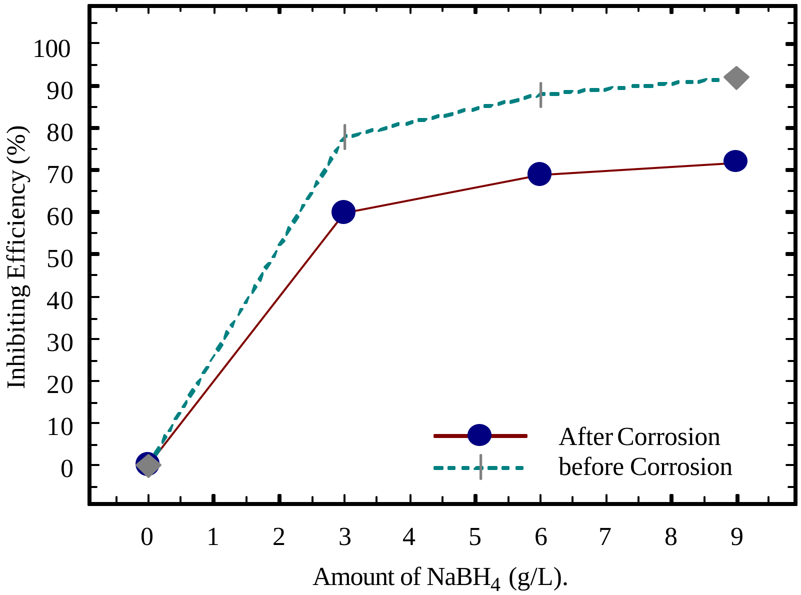


Figure 5: Inhibiting efficiency as a function of sodium borohydride concentration.

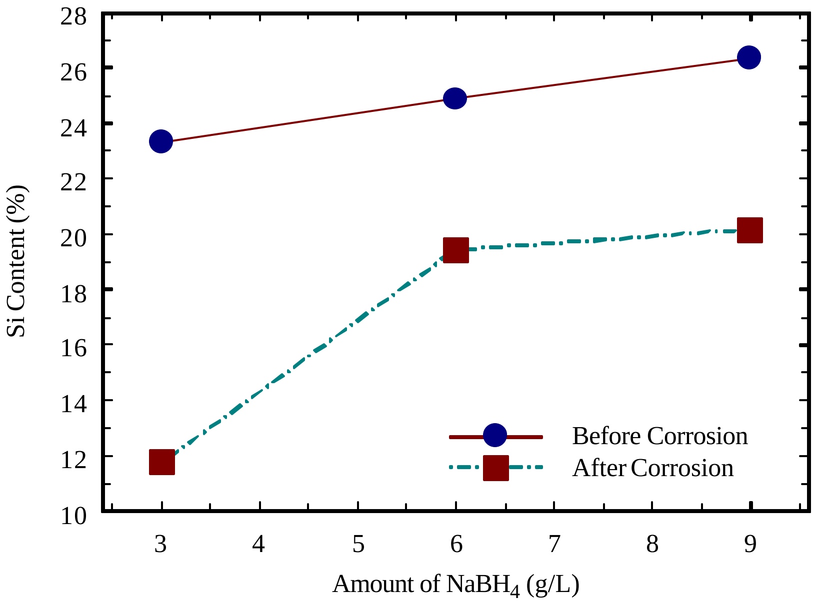


Figure 6: Weight percent of Silica in the deposit as a function of the sodium borohydride concentration

Table 1: Comparison of resistances of deposits prepared by electroless process with different concentration of sodium borohydride

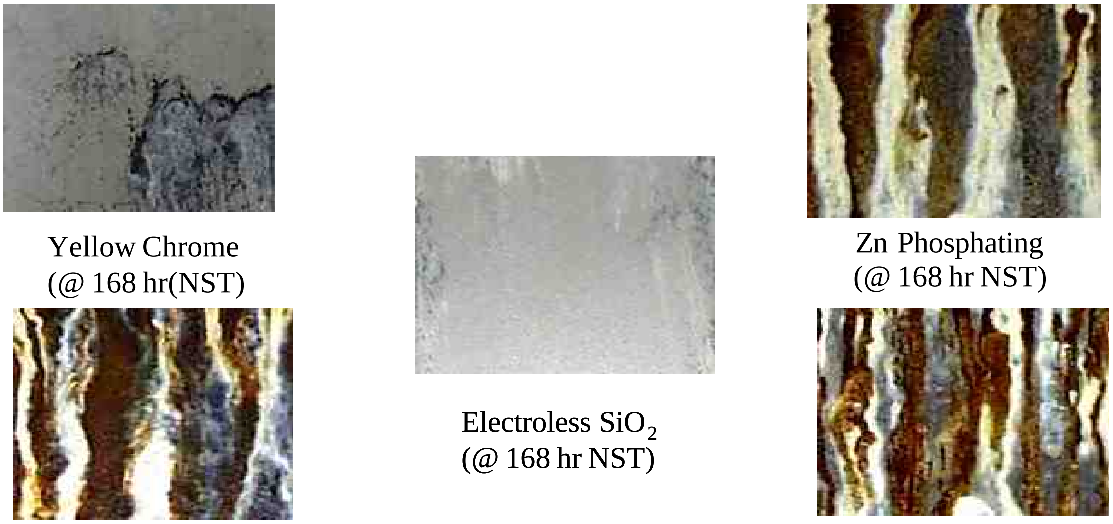
Time	Concentration of Sodium borohydride		
No of days	3 g/L	6 g/L	9 g/L
Initial	1870.1	1941.5	2168.9
1st day	1650.7	1660.2	2071.7
4th day	1072.1	1491.8	1856.2
7th day	830.1	1372.1	1590.1

Values of silica content after corrosion indicate that the silica content decreases rapidly for the samples prepared in the absence of sodium borohydride. With increase in the borohydride concentration, the decrease in the silica content due to corrosion decreases. After an addition of 6 g/L of sodium borohydride, the silica content in the deposit stabilizes.

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. Hence the amount of sodium borohydride is optimized to be 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 silicondioxide coated samples. Also, samples coated with other commercially available conversion coatings such as phosphating and chrome passivation were tested for comparison. Table 2 shows the results of the corrosion testing for each of the samples in a salt spray chamber. 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 presented in Table 2). Among the commercially available coatings, passivation with yellow chrome showed better results compared to that of the phosphating and clear chrome processes. With yellow Chrome process, the red rust appeared at 312 h and the sample failed at 360-520 h. But on the control panels coated with silicondioxide based on electroless process, the red rust appeared after 552 h and the sample failed at 600 h. With the presence of a thin silicondioxide layer, the salt spray corrosion time extends to nearly ten times over the untreated galvanized steel panel. Figure 5 shows the appearance of the galvanized steel panels coated with different coatings subjected to accelerated corrosion in a salt spray chamber. A comparison of the appearance of the panels show the superior performance of the silicondioxide based coating prepared by electroless method.



Yellow Chrome
(@ 168 hr(NST)

Zn Phosphating
(@ 168 hr NST)

Electroless SiO_2
(@ 168 hr NST)

Clear Chrome
(@ 96 hrs NST)

Zn + Phos + Foe
(@ 96 hrs NST)

Figure 7: Appearance of different conversion coatings under accelerated corrosion in a salt spray chamber. The electroless SiO_2 was prepared from a 1:3 PQ bath in the presence of 6 g/L of $NaBH_4$ at 75 ^{o}C for 15 minutes.

Table 2: Comparison of salt spray hours for different coatings under accelerated corrosion

Coating	Time in hours		
	White rust	Red rust	Fail
Zn+Phos+Foe	24	72	96
Zn+Phos	24	72	96
Clear Chromate	24	48	120
Yellow Chromate	144	312	576
Electroless SiO_2	144	552	600

CONCLUSION

A novel non chrome electroless process for the deposition of silica films has been developed. ESCA studies reveal that silicondioxide 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. We have been able to mimic the zinc disilicate layer formed by the Elisha mineralization process. The operating parameters for the electroless process like the concentration of the PQ solution to be used and the amount of reducing agent sodium borohydride were optimized based on the corrosion characteristics of the coatings. Samples prepared from 1:3 PQ solutions at 75 ^{o}C for 15 minutes 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 few commercially available conversion coatings.

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