Phosphate and chromate-based conversion coatings are widely used to decrease the dissolution of sacrificial deposits such as Zn and Zn alloys. Among them, chrome passivates are widely preferred due to their high corrosion resistance, barrier, and self-healing properties, and the ease with which they are applied. However, chrome passivates are generally prepared from hexavalent chromium-based bath, which is known for its toxicity. Governing bodies such as the Environmental Protection Agency and the European Union have issued stringent regulations for the use of hexavalent chromium and its salts in automobiles to facilitate recycling. Several chrome alternatives are currently explored worldwide.

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the white rust, red rust, and the failure of the samples were observed as a function of time. The basis for the failure criterion was determined as 5% red rust on the surface of the samples.

Surface morphology of the coatings was analyzed by viewing them under an ESEM FEI Quanta 200 microscope. Constitutive elements on the surface of the panels were analyzed using energy-dispersive analysis with X-rays (EDAX). X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), was used to analyze the nature of the coating. ESCA results were obtained using a Hewlett-Packard 5950 A ESCA spectrometer which is capable of generating monochromator X-rays. ESCA results were obtained using a Hewlett-Packard 5950 A ESCA spectrometer which is capable of generating monochromator X-rays. The ability of ESCA to generate accurate binding energies is reflected by these results:

\[ \text{Au } 4f_{7/2} = 83.95 \pm 0.05 \text{ eV} \]

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The thickness and microstructure of the silica coating were analyzed by cross-sectional studies at high magnification under SEM. Figure 3 shows the cross-sectional SEM image of the galvanized steel panel coated with silica by the electroless process. A homogenous and dense silica layer tightly anchored to the zinc substrate is observed. The thickness of the silica layer deposited is approximately 500–600 nm. Also, the resistance is comparable to that of commercially available passivates such as dark yellow chrome. The polarization resistance value is comparable to that of the silica deposit obtained by the electrolytic process. Silica layers deposited using the electroless process are highly reproducible and have a 5 times higher polarization resistance than bare galvanized steel (286 \( \Omega \) cm\(^2\)). Also, the resistance is comparable to that of commercially available passivates such as dark yellow chrome (1539 \( \Omega \) cm\(^2\)).

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ESCA results and mechanism of silica deposition.— The coatings were characterized by using a variety of ESCA peak positions. The resulting binding energy for the Si (2p) peak was the main basis for our study. Figure 4a shows the Si (2p) binding energy spectrum obtained for the first thin layer over metallic zinc. Also shown in this figure is the ESCA spectrum for the bare galvanized steel. For the first layer over metallic zinc, the observed binding energy was close to 102.2 eV, which corresponds to Si found exclusively in a disilicate form. The natural zinc disilicate, the hemimorphite form, has a binding energy of 101.8 eV. The value of

Figure 2. Linear polarization plot for bare galvanized steel, galvanized steels coated with silica, and dark yellow chrome.
102.2 eV observed in this study corresponds to disilicate species which exhibit Si (2p) orbital shifts as found in polymerized species.\textsuperscript{17-19} A transition from monomeric to polymeric species results in a decrease of the covalency of the Si–O bonds, while the Si 2p binding energy increases. Based on these results, the first layer corresponds to that of a thin zinc disilicate. The thickness of this layer is approximately 30–50 nm.

The formation of zinc disilicate can be explained through a simple adsorption process. SiO\textsubscript{2} dissolves in water to form monomeric Si(OH)\textsubscript{4} species. The amount of the SiO\textsubscript{2} hydrolyzed to Si(OH)\textsubscript{4} depends on the pH and temperature of the silicate solution. The equilibrium between SiO\textsubscript{2} and silica monomer is given by Eq. 1

\[
\text{SiO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{Si(OH)}_4
\]

According to Iler,\textsuperscript{20} the monomeric species Si(OH)\textsubscript{4} condenses on any 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 study, the Zn substrate is immersed in alkaline sodium silicate solution with a pH of approximately 10.5–11.0. Pourbaix diagrams show that zinc dissolves at this pH as zincate and bizzincate ions.\textsuperscript{21} The surface of the Zn substrate is covered with a thin layer of Zn hydroxide Zn(OH)\textsubscript{2}. The monomeric Si(OH)\textsubscript{4} species react with the receptive surface to form zinc silicate by the following reaction

\[
\text{Si} + \text{OH} + \text{Zn(OH)}_2 \rightarrow \text{Zn} + \text{Si(OH)}_4 + \text{H}_2\text{O}
\]

Thus, a thin layer of zinc disilicate is formed by an adsorption process and the reaction proceeds throughout the available receptive surfaces.

As shown in Fig. 4b, for the second layer, the binding energy of Si (2p) shifts to greater values of 103.3 eV, and 532.7 eV for O (1s), indicating the presence of SiO\textsubscript{2}. The thickness of the SiO\textsubscript{2} layer is 500 nm. Once the receptive surface is covered by zinc disilicate, further growth of the silica is a molecular deposition of SiO\textsubscript{2}. The mechanism for the molecular deposition of SiO\textsubscript{2} from Si(OH)\textsubscript{4} is a condensation reaction catalyzed by the presence of OH groups in which two silanol groups of silicic acid condense to form siloxane groups with the removal of water

\[
\text{Si} - \text{OH} + \text{Si} - \text{OH} \rightarrow \text{Si} - \text{O} + \text{Si} - \text{O} + \text{H}_2\text{O}
\]

Thus, the removal of water or the dehydration process catalyzes this reaction. In the electroless process the removal of the water at the interface takes place through the following reaction

\[
\text{NaBH}_4 \rightarrow \text{Na}^+ + \text{BH}_4^-
\]
\[
\text{BH}_4^- + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{BO}_2^-
\]
\[
\text{BO}_2^- + \text{Na}^+ \rightarrow \text{NaBO}_2
\]

The operating temperature of 75°C increases both the dehydration process and the kinetics of sodium borohydride decomposition. The condensation proceeds until a predominant amount of available silanol groups are used up for the production of siloxane bonds. 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 silicon dioxide over zinc disilicate.

The concentration of monomeric species, the rate of dehydration at the metal electrolyte interface, operating temperature, and pH of the bath are critical for the formation of uniform deposits. The role of the above parameters on uniformity and silica content in the deposit were studied to develop a corrosion-resistant silicate coating.

**Effect of bath temperature.**— Operating temperature of the bath plays a significant role in the deposition of silica. To analyze the effect of bath temperature, samples were prepared in a 1:8 sodium silicate/water solution with 5 g/L of NaBH\textsubscript{4} at various bath temperatures. Figure 5 shows the variation in the silica content and the polarization resistance of the coating deposited at various bath temperatures. The polarization resistance of the coatings was determined by linear polarization. The deposits prepared at room tem-
In alkaline sodium hydroxide and potassium hydroxide solutions, monomeric silica. Extensive studies exist on the passivation of zinc, formation of a passive film on the surface followed by adsorption of metal. This disrupts the formation of a uniform silicate layer on the zinc substrate is directly dependent on the amount of sodium silicate in the deposition bath. Different sodium silicate and water ratios such as 1:8, 1:5, 1:3, and 1:1 (v/v mix) were used to form the silicate layer. The depositions were performed for 15 min in the presence of 5 g/L NaBH4 at a bath temperature of 75°C. Table I summarizes the average polarization resistance and silica content as a function of the sodium silicate to water bath at different pH values. The temperature of the bath was 25°C. For the panel immersed in pH 10.5, the OCP values tend to more noble values due to the formation of passive film on the surface. With increase in pH, the formation of the passive film is affected and a less stable film is observed for a sample with pH 11.0. Further increase in pH to 12 leads to active metal corrosion.

Figure 5. Average polarization resistance and silica weight percent of the deposits as a function of operating bath temperature. Deposition was done in 1:8 sodium silicate/water solution and 5 g/L of sodium borohydride.

Effect of pH.—The present inventive process is based on the formation of a passive film on the surface followed by adsorption of monomeric silica. Extensive studies exist on the passivation of zinc in alkaline sodium hydroxide and potassium hydroxide solutions. In moderately alkaline solutions of pH 10.5, zinc forms passive films which reduce the rate of metal dissolution. Increasing the pH above 10.5 has a tendency to dissolve the passive film formed and increase active metal corrosion. Figure 6 shows the open-circuit potentials (OCPs) of galvanized steel panels in 1:8 sodium silicate/water bath at different pH values. The temperature of the bath was 75°C. For the panel immersed in pH 10.5, the OCP values tend to more noble values due to the formation of passive film on the surface. With increase in pH, the formation of the passive film is affected and a less stable film is observed for a sample with pH 11.0. Further increase in pH to 12 leads to active metal dissolution of the zinc film. This disrupts the formation of a uniform silica coating, especially the formation of the first zinc disilicate layer. The formation of poor silica film on the surface of the galvanized steel is reflected on the corrosion behavior of the coatings. Linear polarization study shows that for samples prepared at pH 10.5, the polarization resistance is 1432 Ω cm², in comparison with 720 Ω cm² for a sample prepared at pH 12.0. Also, the concentration of monomeric species, namely, Si(OH)4, is a strong function of bath pH. The sodium silicate solution is a complex mixture of various silicate ions, such as Si(OH)4, HSiO3−, SiO3²−, Si3O7⁶−, and HSi3O10⁶−. Figure 6b shows the pH concentration diagram for various silicate species in equilibrium in sodium silicate solution. The concentration of various silicate species in the bath were determined by using several elemental balances and equilibrium conditions at a specified pH. The calculations are summarized and shown in the Appendix. Based on the calculations, we find that silica primarily exists as anions at pH greater than 10.0. At pH values lower than 10.0, the Si(OH)4 concentration exceeds the solubility limit and becomes a gel. Experimental efforts to decrease the pH of the solution to less than 10.0 confirm this finding. Figure 6b shows that the concentration of Si(OH)4 decreases with increase in pH and is negligible beyond a pH of 11.0. The concentration of Si(OH)4 is crucial for the formation of an impermeable zinc disilicate layer followed by condensation of the SiO2 layer. Thus bath pH should be maintained at a favorable value of 10.5 for two reasons: (i) formation of stable passive films and (ii) high concentration of Si(OH)4 for the silica deposition to commence.

Effect of sodium silicate concentration.—The successful formation of a uniform silicate layer on the zinc substrate is directly dependent on the amount of sodium silicate in the deposition bath. Different sodium silicate and water ratios such as 1:8, 1:5, 1:3, and 1:1 (v/v mix) were used to form the silicate layer. The depositions were performed for 15 min in the presence of 5 g/L NaBH4 at a bath temperature of 75°C. Table I summarizes the average polarization resistance and silica content as a function of the sodium silicate concentration in the bath. The increase in thickness and the corresponding weight percent increase in the silica show that silica deposition is favored with increase in concentration of sodium silicate in the bath. The concentration of the monomeric species increases by increasing the concentration of sodium silicate in the solution, thus favoring silica formation. Silicate deposition with 1.5 μm thickness was obtained with use of a concentrated bath. Also, the polarization resistance of the deposit increases with concentration. The observed increase of polarization resistance is attributed to the increased
amount of silica deposited. High polarization resistance of 2057 $\Omega\text{ cm}^2$ was obtained with the use of 1:1 sodium silicate/water solution. However, a 1:1 sodium silicate/water bath was more viscous, leading to difficulty in handling. Hence, a 1:3 sodium silicate/water bath was used for further studies. Another important observation made was the development of superficial microcracks as observed in SEM (not shown) for concentrations beyond 1:8 (sodium silicate/water). The amount of cracks formed was found to increase with increase in thickness of the silica deposited. The influence of these cracks on the corrosion resistance offered by silica coatings is discussed later.

**Effect of sodium borohydride concentration.**— The effect of sodium borohydride concentration on the coating performance was studied. The deposition was carried out on galvanized steel panels at 75°C for 15 min from 1:3 sodium silicate/water solution. However, a 1:1 sodium silicate/water bath was used for further studies. Another important observation made was the development of superficial microcracks as observed in SEM (not shown) for concentrations beyond 1:8 (sodium silicate/water). The amount of cracks formed was found to increase with increase in thickness of the silica deposited. The influence of these cracks on the corrosion resistance offered by silica coatings is discussed later.

**Table I. Effect of sodium silicate concentration on polarization resistance and Si content of deposits prepared by the electroless process.**

<table>
<thead>
<tr>
<th>Sodium silicate/water</th>
<th>Silica content (wt %)</th>
<th>Polarization resistance ($\Omega\text{ cm}^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:8</td>
<td>13.7</td>
<td>1432</td>
</tr>
<tr>
<td>1:5</td>
<td>19.1</td>
<td>1661</td>
</tr>
<tr>
<td>1:3</td>
<td>24.8</td>
<td>1941</td>
</tr>
<tr>
<td>1:1</td>
<td>28.3</td>
<td>2057</td>
</tr>
</tbody>
</table>

**Table II. Comparison of polarization resistance of deposits prepared by the electroless process with different concentrations of sodium borohydride.**

<table>
<thead>
<tr>
<th>Time (No. of days)</th>
<th>0 g/L</th>
<th>3 g/L</th>
<th>6 g/L</th>
<th>9 g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1323</td>
<td>1870.1</td>
<td>1941.5</td>
<td>2168.9</td>
</tr>
<tr>
<td>1st day</td>
<td>632.1</td>
<td>1650.7</td>
<td>1660.2</td>
<td>2071.7</td>
</tr>
<tr>
<td>4th day</td>
<td>601.1</td>
<td>1072.1</td>
<td>1491.8</td>
<td>1856.2</td>
</tr>
<tr>
<td>7th day</td>
<td>560</td>
<td>830.1</td>
<td>1372.1</td>
<td>1590.1</td>
</tr>
</tbody>
</table>

**Figure 7.** CVs of silica-coated samples prepared with different concentrations of sodium borohydride in a 1:3 sodium silicate/water solution. Comparison with bare galvanized steel panel is shown in the inset.

**Figure 8.** Silica content as a function of NaBH₄ concentration. Deposition was done in 1:3 sodium silicate/water solutions.
Corrosion and stability of silica coatings.— The silica deposited is porous in nature and is not impermeable. The stability of silica-coated panels in different media was tested through polarization resistance measurements. Two samples were immersed in 0.5 M Na2SO4 solution, pH 4.0, and distilled water. Another sample was left exposed in air. The polarization resistance was measured by linear polarization at regular intervals in a 0.5 M Na2SO4 solution. The depositions were performed in 1:3 bath for 15 min in the presence of 6 g/L NaBH4, at a bath temperature of 75°C. Figure 10a shows the polarization resistance as a function of time of exposure. It is seen that samples exposed in air do not undergo any corrosion and the polarization resistance remains the same over a period of 1 week. However, for samples immersed in aqueous media, significant decrease in polarization resistance is observed. Figure 10b shows an SEM image of a silica-coated electroless galvanized steel panel before corrosion and after corrosion in water for 1 week. As mentioned before, superficial cracks were present for samples prepared from 1:3 bath. For the samples immersed in water for 1 week, white spongy particles were found on the surface of the coating. EDAX spot analysis shows that they are corrosion products of zinc. Despite the formation of corrosion products, the silica coating is still intact. Also, the corrosion product does not proceed uniformly across the surface. They are predominantly found near the cracks. Unlike hexavalent chrome passivates, the silica coatings do not exhibit any self-healing mechanism. Instead, the corrosion products are expected to accumulate in the porous silicate coating, inhibiting further corrosion of the underlying zinc substrate. A similar phenomenon was also observed by Dalbin et al.15 However, in the present case, the use of sodium borohydride produces dense silica films and offers improved stability for the silica coating. Despite the different protection mechanism, the silica coatings provide equivalent or better corrosion protection than chrome passivates, as observed from the salt spray chamber tests.

Conclusion

A novel nonchrome electroless process for the deposition of silica films has been developed. ESCA studies revealed that the coating is composed of two layers, an underlying zinc disilicate layer and a thick silicon dioxide layer. An adsorption-condensation mechanism is proposed to account for the two-layer silicate formation. Decomposition of reducing agent (sodium borohydride) catalyzes silica deposition by consuming water at the metal–electrolyte interface. The operating parameters for the electroless process such as the concentration of the sodium silicate solution, operating tem-

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Table III. Results of ASTM B117 accelerated corrosion testing for various coatings.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Time of exposure (hour)</th>
<th>White rust</th>
<th>Red rust</th>
<th>Fail</th>
</tr>
</thead>
<tbody>
<tr>
<td>Galvanized steel</td>
<td>24</td>
<td>48</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>Galvanized steel/phosphating</td>
<td>48</td>
<td>144</td>
<td>192</td>
<td></td>
</tr>
<tr>
<td>Galvanized steel/clear chrome</td>
<td>24</td>
<td>48</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>Galvanized steel/dark yellow chrome</td>
<td>144</td>
<td>312</td>
<td>560</td>
<td></td>
</tr>
<tr>
<td>Galvanized steel/silica</td>
<td>144</td>
<td>552</td>
<td>600</td>
<td></td>
</tr>
</tbody>
</table>

---

Figure 9. (a) Linear polarization plots for various coatings. (b) Comparison of corrosion rate of various coatings.
temperature, and the amount of reducing agent (sodium borohydride) were optimized based on the corrosion protection performance of the coatings. Comparison of the corrosion data from the salt spray chamber shows the improved performance of the silicon dioxide coating compared to other commercially available conversion coatings. This process can also be applied to other substrates such as iron and aluminum.

Acknowledgment
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Appendix
The sodium silicate solution obtained from PQ Corp. is 37.5 wt % solution with SiO₂/Na₂O in a molar ratio of 3.22. The silica solution is a complex mixture of various species. The variables to be determined are as follows: [Si(OH)₄]⁻, [HSiO₃]⁻, [Si₂O₅]⁻, [H₂SiO₆]⁻, [Si(OH)₂]⁻, [H₂SiO₆]⁻. The concentration of the [H⁺] depends on the specified pH. The equations used to determine the equilibrium concentrations are:

Material balance on Si

Equilibrium conditions Si(OH)₄ and H₂SiO₆

These equations were solved simultaneously using Maple. The various rate constants used in the equations are as follows: k₁ = 10⁻⁷.8, k₂ = 10⁻¹².8, k₃ = 2200, k₄ = 10⁻⁹.8, k₅ = 10⁻¹².8, and k₆ = 10⁻¹².8.  

References