Development of an Electroless Method to Deposit Corrosion-Resistant Silicate Layers on Metallic Substrates

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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.

Soluble silicates are economical and environmentally friendly and have been used for several decades to protect metals. They form a thin protective film on various metal surfaces. Corrosion-resistant coating of colloidal silica along with hexavalent and trivalent 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 at a background pressure of \( <5 \times 10^{-9} \) Torr. The ability of ESCA to generate accurate binding energies is reflected by these results: Au 4f\(_{7/2}\) = 83.95 ± 0.05 eV and C (1s) = 284.4 ± 0.1 eV for graphite. The materials under study were all oxide insulators and thus produced significant charging shifts, which were removed by using a low-energy electron flood gun. This procedure, described in detail elsewhere\(^{16}\) was successfully used in many related silicate studies.\(^{17,18}\)

**Results and Discussion**

Initially, silica was deposited from an aqueous solution of sodium silicate diluted eight times in water (v/v) in the presence of sodium borohydride. The concentration of the reducing agent, sodium borohydride (NaBH\(_4\)), was 5 g/L. Deposition was performed at 75°C for 15 min. Subsequent to deposition, the samples were dried in air at room temperature for 24 h and then rinsed with distilled water. Visual observation showed a smooth, transparent glassy silica deposit. Figure 1a is a scanning electron microscopy (SEM) image of a galvanized steel panel coated with silica and shows well-defined hexagonal structures which are characteristic of zinc deposit. The silica coating reproduces the surface morphology of the underlying zinc substrate, indicating the uniformity of the thin layer of silica deposit. Figure 1b shows the EDAX spectrum of the above-mentioned sample. The EDAX method was used to obtain a relative estimate of the silica deposited.\(^{14}\) The average silica content in the deposit was found to be approximately 13.7 wt % with 86.3% being zinc. Linear polarization studies in a 0.5 M Na\(_2\)SO\(_4\) (pH 4.0) solution were performed on several spots of the silicat ed sample to estimate the polarization resistance (\(R_p\)), also referred to as corrosion resistance. Figure 2 shows the linear polarization plot for bare galvanized steel and silica-coated galvanized steel. Also shown for comparison is the galvanized sample coated with a commercially available passivate such as dark yellow chrome. The polarization resistance measured by the linear polarization method for the silica-coated samples was 1432 Ω cm\(^2\). The polarization resistance value is comparable to that of the silica deposit obtained by the electrolytic process.\(^{14}\) Silica layers deposited using the electrol process are highly reproducible and have a 5 times higher polarization resistance than bare galvanized steel (286 Ω cm\(^2\)). Also, the resistance is comparable to that of commercially available passivates such as the dark yellow chrome (1539 Ω cm\(^2\)).

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 electrol 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 cross section reveals the presence of two distinct layers, a thin layer immediately over metallic zinc followed by a thick layer. ESCA studies were performed to analyze the metal–silicate interface and the deposition mechanism.

**ESCA results and mechanism of silica deposition.**— The coatings were characterized by using a variety of ESCA peak positions.\(^{14,18}\) The resulting binding energy for the Si (2p) peak was the main basis for our study.\(^{18}\) 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.\(^{18}\) The natural zinc disilicate, the hemimorphite form, has a binding energy of 101.8 eV. The value of
102.2 eV observed in this study corresponds to disilicate species which exhibit Si (2p) orbital shifts as found in polymerized species. 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. SiO₂ dissolves in water to form monomeric Si(OH)₄ species. The amount of the SiO₂ hydrolyzed to Si(OH)₄ depends on the pH and temperature of the silicate solution. The equilibrium between SiO₂ and silica monomer is given by Eq. 1

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

According to Iler, the monomeric species Si(OH)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 bizincate ions. The surface of the Zn substrate is covered with a thin layer of Zn hydroxide Zn(OH)₂. The monomeric Si(OH)₄ species react with the receptive surface to form zinc silicate by the following reaction

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

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 SiO₂. The thickness of the SiO₂ layer is 500 nm. Once the receptive surface is covered by zinc disilicate, further growth of the silica is a molecular deposition of SiO₂. The mechanism for the molecular deposition of SiO₂ from Si(OH)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

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

\[ \text{NaBH}_4 \rightarrow \text{Na}^+ + \text{BH}_4^- \]
\[ \text{BH}_4^- + 2\text{H}_2\text{O} \rightarrow 4\text{H}_2 + \text{BO}_3^2^- \]
\[ \text{BO}_3^2^- + \text{Na}^+ \rightarrow \text{NaBO}_3 \]  

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 NaBH₄ 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, namely, Si\(^{4+}\) prepared at pH 12.0. Also, the concentration of monomeric species, Si\(^{4+}\), increases by favoring silica formation. Silicate deposition with 1.5 wt% of silica was observed when deposited at a bath temperature of 75°C. Significant increase in the silica deposition was observed beyond a bath temperature of 50°C. This agrees with the previous findings of Iler\(^{20}\) that silica formation is favored in hot solutions. Also, by increasing the bath temperature one increases the reaction rate of sodium borohydride, which catalyzes the silica deposition reaction. At temperatures higher than 75°C, no significant increase in silica content was observed. The polarization resistance for the deposit prepared at room temperature was 300 \(\Omega\) cm\(^2\), which is similar to that of a bare galvanized steel sample. Deposits prepared at 75°C show polarization resistance value of 1432 \(\Omega\) cm\(^2\). The observed increase in the polarization resistance is due to the formation of dense silica deposits.

**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.\(^{22}\) 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.\(^{21}\) 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 dissolution of the zinc metal. This disrupts the formation of a uniform silica coating, especially in 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 \(\Omega\) cm\(^2\), in comparison with 720 \(\Omega\) cm\(^2\) 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)\(_4\), HSiO\(_3\), SiO\(_2\)\(_3\)\(^{2-}\), H\(_2\)Si\(_2\)O\(_5\)\(^{2-}\), and H\(_2\)Si\(_3\)O\(_8\)\(^{3-}\). 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 SiO\(_2\) 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 NaBH\(_4\) 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 \(\mu\)m 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. The borohydride concentration was varied between 3 and 9 g/L. The treated samples were dried in air for 24 h and rinsed in distilled water. The surface coverage of silicate coatings for different concentrations of sodium borohydride was estimated using cyclic voltammetry (CV).

CV studies were done in a three-electrode setup using an SCE in 0.5 M \( \text{Na}_2\text{SO}_4 \), pH 4.0. The voltammograms were obtained by recording the current while varying the applied potential in the potential window of −1.6 to −0.8 V vs SCE. The scan rate was 5 mV/s. Figure 7 shows the CVs obtained for silicate samples prepared with different concentrations of sodium borohydride. The voltammograms obtained in comparison with bare galvanized steel are shown in the inset of Fig. 7. Because the currents depend on available bare surface of the substrate and it is proportional to the amount of material lost from the surface, CVs can be used to obtain a qualitative estimate for the inhibiting efficiency of silica coating toward corrosion. The peak reduction current and the maximum in the oxidation current decrease rapidly for silica-coated samples when compared to bare zinc samples. The observed large decrease in current in Fig. 7 is approximately 78% for 3 g/L and 92% for 9 g/L of borohydride. This indicates that the coating functions as a barrier film and decreases the dissolution of the underlying substrate significantly. Barrier protection of silica coating increases with the concentration of sodium borohydride.

The sodium borohydride concentration was optimized based on the polarization resistance and stability of the coatings. The deposits were prepared from 1:3 sodium silicate/water electrolyte in the presence of different concentrations of sodium borohydride. To estimate the role of sodium borohydride, deposits were also prepared in the absence of sodium borohydride in the electrolyte. The polarization resistance was measured in a 0.5 M \( \text{Na}_2\text{SO}_4 \) solution, pH 4.0. After measuring the initial polarization resistance, the stability of the coating was tested by immersing the samples in distilled water for over a span of 1 week. The polarization resistance was measured at regular intervals and the values are summarized in Table II. The silica content was analyzed using EDAX before and after immersion in water for 1 week.

As shown in Table II, the polarization resistance and stability of the coating increases with the increase of the concentration of sodium borohydride. The samples prepared in the absence of sodium borohydride have initial polarization resistance of 1323 \( \Omega \text{ cm}^2 \), which is comparable to that of the chrome passivates. However, the stability of the coating in aqueous media is very low. The average polarization resistance drops to 630 \( \Omega \text{ cm}^2 \) after the samples were exposed in aqueous media for a period of 24 h. The samples prepared in the presence of 6 g/L of sodium borohydride have a polarization resistance of 1372 \( \Omega \text{ cm}^2 \), even after immersion in water for 160 h. The observed increase in stability of the deposits can be attributed to the removal of the water at the panel interface due to sodium borohydride decomposition, which enhances the condensation of the 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 160 h which are presented in Fig. 8. As shown in Fig. 8, the silica weight percent in the deposit increases from 11.75% estimated for 0 g/L of sodium borohydride in the electrolyte to approximately 23% in the presence 3 g/L sodium borohydride.

### 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>Polarization resistance (( \Omega \text{ cm}^2 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 g/L</td>
<td>1323 1870.1 1941.5 2168.9</td>
</tr>
<tr>
<td>1st day</td>
<td>632.1 1650.7 1660.2 2071.7</td>
</tr>
<tr>
<td>4th day</td>
<td>601.1 1072.1 1491.8 1856.2</td>
</tr>
<tr>
<td>7th day</td>
<td>560 830.1 1372.1 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.](image)

![Figure 8. Silica content as a function of NaBH₄ (g/L). Deposition was done in 1:3 sodium silicate/water solutions.](image)
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 temperature, and bath composition are critical factors affecting the coating quality.

**Conclusion**

The silica coating provides a significant advantage in terms of corrosion protection compared to traditional chrome passivation methods. The corrosion resistance and stability of these coatings are superior, even under accelerated corrosion conditions. The incorporation of silica coatings in commercial applications for corrosion protection is promising, offering a sustainable and environmentally friendly alternative to chrome passivation.

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>

This table summarizes the corrosion performance of various coatings at different exposure times.

**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 test solution of 0.5 M Na₂SO₄, pH 4.0. 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. 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.

**Corrosion performance in comparison with commercial coatings.**—Since the objective of the present work is to substitute the toxic chromate processes with environmentally friendly coatings, it is imperative to analyze the corrosion properties of silica coatings and compare them with the commercial passivation processes. Figure 9a shows a comparison of linear polarization responses obtained for electroplated zinc panels and electroplated steel panels coated with conversion coatings such as phosphate, chrome passivates, and silica coatings prepared by the electroless method. The polarization resistance values are very low (286 Ω cm²) for galvanized steel panels in the absence of conversion coating, indicating a rapid dissolution under corroding conditions. The highest polarization resistance values were estimated for silica coatings, indicating that these coatings have much better barrier properties when compared to the other commercial conversion coatings. The corrosion rate of these coatings is evaluated from the polarization resistance. The Stearn–Geary equation was used to evaluate the corrosion current and corrosion rate of these coatings. An approximate corrosion rate is calculated from the polarization resistance values estimated for silica coatings, in comparison to other commercial conversion coatings. The failure criterion was 5% surface coverage with red rust. Galvanized steel sample without any passivation or coating failed in a span of 48 h. Among the commercially available coatings, the passivation with dark yellow chrome showed better results compared to that of phosphating and clear chrome processes. With the yellow chrome process, the red rust appeared at 312 h, failing after 560 h, but on the control panels coated with silica coatings, the red rust appeared at 552 h, failing after 600 h. In the presence of a thin silica layer, the salt spray corrosion time extends to nearly 10 times over the untreated galvanized steel panel. A comparison of the corrosion data of the panels shows the improved performance of the silicon dioxide-based coating prepared by electroless method.
Figure 10. (a) Variation of polarization resistance of silica-coated galvanized steel as a function of time in various media. (b) SEM micrograph of silica-coated galvanized steel before and after immersion in distilled water for 1 week.

perature, 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.

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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 total silica concentration is 6.625 M. The silicate bath is a complex mixture of various species. The variables to be determined are the concentrations of the $\text{H}^+$ and $\text{OH}^-$ ions, as well as the concentrations of the various silicon species present in the bath. These equations were solved simultaneously using Maple. The various rate constants used in the equations are as follows:

$$
\text{Si}_2\text{O}_5^{2-} + 2\text{H}^+ \rightarrow 2\text{H}_2\text{SiO}_3
$$

$$
\text{Si}_2\text{O}_5^{2-} + \text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SiO}_3
$$

$$
\text{Si}_2\text{O}_5^{2-} + \text{OH}^- \rightarrow 2\text{H}_2\text{SiO}_3
$$

$$
\text{Si}_2\text{O}_5^{2-} + \text{H}^+ \rightarrow 2\text{H}_2\text{Si}\text{O}_3
$$

$$
\text{Si}_2\text{O}_5^{2-} + \text{H}_2\text{O} \rightarrow 2\text{H}_2\text{Si}\text{O}_3
$$

$$
\text{Si}_2\text{O}_5^{2-} + \text{OH}^- \rightarrow 2\text{H}_2\text{Si}\text{O}_3
$$

$$
\text{Si}_2\text{O}_5^{2-} + \text{H}^+ \rightarrow 2\text{H}_2\text{Si}\text{O}_3
$$

The equations were solved simultaneously using Maple. The various rate constants used in the equations are as follows: $k_1 = 10^{-9.8}$, $k_2 = 10^{-12.16}$, $k_3 = 2200$, $k_4 = 10^{-9.8}$, and $k_5 = 10^{-12.1}$.

References