# Technical Article

# The Corrosion Behavior of Cadmium, Zinc, Zinc-Nickel & Nickel-Phosphorus/Zinc Commercial Coatings in Chloride Solutions

by L.A.S. Silva & L. Sathler

This work relates to the corrosion resistance of cadmium replacement coatings. For years, cadmium deposits have been used for their good corrosion resistance and their high lubricity. However, owing to the high toxicity of cadmium, alternative coatings have been proposed and zinc alloy coatings are generally indicated. Cadmium, zinc, zinc-16.3% nickel and electroless nickel-6% phosphorus + zinc heat treated at 320°C (608°F) for 1 hr were evaluated. The deposits were produced from commercial baths applied over carbon steel substrates. The coatings were examined by scanning electron microscopy (SEM) and evaluated



Fig. 1-Electron micrographs of the surface deposits: a) Cd, b) Zn.

#### Nuts & Bolts: What This Paper Means to You

Cadmium replacements have been an important issue for several years. Many substitutes have been developed and used with varying degrees of success. This work takes the most important ones ... zinc, zinc-nickel and zinc over electroless nickel ... and examines them with the same yardstick.

by salt spray, total immersion and anodic polarization tests in 3% NaCl solutions. Cadmium coatings with chromate showed thin grains and an excellent resistance both to salt spray and to electrochemical tests. Zinc coatings with chromate and electroless Ni-6%P + zinc, heat treated at 320°C (608°F) showed microcracks, rough grains and a lower corrosion resistance than the cadmium coatings. Zn-16.3% Ni coatings with chromate showed thin grains and a superior behavior to cadmium coatings. The Zn-16.3% Ni alloy coating could replace cadmium deposits in sodium chloride solutions, at room temperature.

Cadmium coatings have good weldability, low electrical contact resistance, a low torque-tension ratio, high lubricity and good corrosion resistance.<sup>1,2</sup> However, because of the inherent toxicity of cadmium,<sup>1,3</sup> alternative coatings have been proposed. Among them, zinc alloy deposits are generally used.<sup>1,3-6</sup> Zinc-nickel coatings are used in a large number of applications. Prior work<sup>7-9</sup> shows that these deposits are more resistant to corrosion than pure zinc deposits from chloride solutions. The nickel content depends on the plating solution and its pH.<sup>8-10</sup> The most common compositions are between 5 and 20% nickel. This work is a study of the corrosion resistance of cadmium, zinc, zinc-nickel and nickel-phosphorus + zinc coatings in chloride solutions.

#### **Experimental Procedure**

The deposits were commercially produced. The substrates used were AISI 1010 carbon steel samples measuring 70 x 50 x 2 mm ( $2.75 \times 2.00 \times 0.79$  in.). The following deposits were studied:

- Cadmium plate with olive drab chromate,
- Zinc plate with olive drab chromate,
- Zinc-16.3% nickel alloy plate with yellow chromate and
- Electroless Ni-P / zinc plate followed by heat treatment at 320°C (608°F) for 1 hr.

\*Corresponding Authors: Luís Alexandre Soares da Silva E-mail: lass@metalmat.ufrj.br Lúcio Sathler E-mail: lsathler@metalmat.ufrj.br Address: PEMM / COPPE Universidade Federal do Rio de Janeiro P.O. Box 68505 21945-970, Rio de Janeiro, Brazil Before plating, the samples were degreased in toluene and then in alkaline solution at 70°C (158°F). They were then cleaned in distilled water, stripped, cleaned again, neutralized and cleaned once more. Cadmium was plated from a cyanide bath between 25 and 45°C (77 and 113°F) at a current density of 5.0 A/dm<sup>2</sup> (46.4 A/ft<sup>2</sup>). Zinc was also plated from a cvanide bath between 25 and 45°C (77 and 113°F) at 2.0 to 3.0 A/dm<sup>2</sup> (18.6 to 27.9 A/ft<sup>2</sup>). The zinc-16.3% nickel alloy was deposited from an acid bath at 25 and 45°C (77 and 113°F) at 7.0 A/dm<sup>2</sup> (65 A/ft<sup>2</sup>). Electroless Ni-P deposition was done in a hypophosphite acid bath at 80 to 90°C (176 to 194°F), followed by zinc electrodeposition from a cyanide bath. All the coatings were baked at 190°C (374°F) for 3 hr for relief of hydrogen embrittlement. The deposit thicknesses were measured by the magnetic induction method.\* The average thickness values were:

•	Cadmium:	$10.4 \ \mu m \ (0.41 \ mil)$
•	Zinc:	26.8 µm (1.06 mil)

- Zinc -16.3% nickel: 12.0 µm (0.47 mil)
- Electroless Ni-6%P + zinc:  $11.0 \ \mu m \ (0.43 \ mil).$

The surface morphology of the deposits was examined by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS).

The following corrosion tests were performed:

- *Salt spray test* (ASTM B117). Twelve specimens of each coating were used, one of which was scratched. Observations were made at 24, 48, 72, 96, 115, 138, 206, 253, 302, 374, 444, 542, 628, 745, 850 and 950 hr.
- Total immersion (3% NaCl solution with aeration, pH 5.4). Four specimens of each coating and three uncoated carbon steel samples were used. Each material set was immersed in a different cell. A copper wire made electrical contact with the specimen to measure the corrosion potential. A saturated calomel electrode (SCE) was used as a reference electrode. The specimen edges and the copper wire were covered by an insulating lacquer leaving only 54 cm<sup>2</sup> (8.37 in<sup>2</sup>) of surface area exposed to the corrosion solution.
- Anodic and cathodic polarization (3% NaCl solution with aeration, pH 7.0). Potentiostatic curves were measured with a potentiostat-galvanostat<sup>\*\*</sup> using a saturated calomel electrode (SCE) as reference electrode and an AISI 316 stainless steel plate, with an area of 203 cm<sup>2</sup> (31.5 in<sup>2</sup>), as the counter electrode.
- Linear polarization (3% NaCl solution with aeration, pH 7.0). The samples were potentiostatically polarized at ± 5, ± 10 and ± 15 mV from the corrosion potential. The measurements were made in the same cell used for the polarization tests.

Polarization resistance  $(R_p)$  is defined as the slope of the polarization curve at the point corresponding to the corrosion potential where I = 0, or



Fig. 2–Electron micrographs of the surface of the deposits: a) Zn-16.3% Ni; b) Ni-6%P/Zn [320°C (608°F), 1 hr].

# Table 1Salt-spray Test Results (up to 950 hr)

Coating	Chromate?	White Corrosion	Red Corrosion
Cd w/o scratch	Yes	No corrosion	No corrosion
Cd with scratch	Yes	No corrosion	Light (48 hr)
Zn w/o scratch	Yes	Light (374 hr)	Medium (628 hr)
Zn with scratch	Yes	Light (138 hr)	Medium (206 hr)
Zn-Ni w/o scratch	Yes	No corrosion	No corrosion
Zn-Ni with scratch	Yes	No corrosion	Light (374 hr)
Ni-P/Zn w/o scratch	No	Medium (24 hr)	Medium (24 hr)
Ni-P/Zn with scratch	n No	Medium (24 hr)	Heavy (24 hr)

$$R_{p} = \left(\delta E / \delta I\right)_{I=0} \tag{1}$$

The theoretical basis of the method was established by Stern and Geary,<sup>11</sup> who found a relationship between the corrosion current and the polarization resistance, that is:

$$I_{corr} = \frac{b_a \cdot b_c}{2.3(b_a + b_c)} \times \frac{1}{\left(\frac{\partial E}{\partial I}\right)_{i=0}}$$
(2)

where  $b_a$  and  $b_c$  are the anodic and cathodic Tafel constants. This expression above can be written as:

$$I_{corr} = \frac{B}{R_p}$$
(3)

where

$$B = \frac{b_a \cdot b_c}{2.3 \left(b_a + b_c\right)} \tag{4}$$

<sup>\*\*</sup> Fischer Dualscope, Fischer Technology, Inc., Windsor, CT 06095.

<sup>\*\*\*</sup> Omnimetra PG-05, Omnimetra Instrumentos Científicos Ltda., Nova Friburgo, Rio de Janeiro, Brazil.



Fig. 3-Potential variation with time in total immersion tests.



Fig. 4-Anodic polarization curves of the coatings studied.

Some *B* values for metallic materials have been reported by A.Pourbaix.<sup>12</sup> In this work *B* was calculated from  $b_a$  and  $b_c$  values which were determined from the anodic and cathodic polarization curves.

#### Results

Figure 1 shows the cross section of the cadmium deposit at a magnification of 4000X (left photo). The substrate is at the top, the deposit is in the middle and the resin is on the bottom. The SEM surface view of the cadmium (right photo) is shown at a magnification of 2000X. The cadmium deposit (Fig. 1a) (8.6  $\mu$ m) was continuous, fine-grained, smooth and well-chromated (2.0  $\mu$ m), as identified by EDS. The zinc deposit (Fig. 1b) (12.4 µm) exhibited larger grains, but the surface was smooth and well chromated (1.9  $\mu$ m). In cross section, thin cracks were observed across the zinc deposit. Figure 2 shows (at the same magnification) that the Zn-16.3% Ni alloy deposit (Fig. 2a) was irregular, fine-grained and no cracks were seen in the cross section. The electroless Ni-6%P/Zn deposit (Fig. 2b) exhibited an irregular surface, rough grains and microcracks. Energy dispersive x-ray spectroscopy (EDS) of the electroless Ni-6%P/Zn samples heat treated at 320°C (608°F) for 1 hr showed the presence of 6% Ni on the surface.

Table 1 shows the salt-spray test results. The scratched cadmium sample showed some points of red rust after 48 hr of testing but they did not increase with additional time. The scratched Zn - 16.3% Ni deposit sample showed red rust points after 374 hr. They also did not enlarge with added time. The electroless Ni-6%P/Zn with and without the scratch showed white and red rust after 24 hr. These coatings were heavily corroded and were removed from the salt-spray chamber after 138 hr.

Figure 3 shows the potential variation with time in the total immersion tests. The zinc coatings exhibited a potential below –1000 mV during 50 days without corrosion. After that, the potential started to increase reaching –690 mV at the end of 100 days. The samples exhibited a heavy red rust. The cadmium samples did not corrode and the potential remained constant, at about –755

Table 2Results of Anodic & Cathodic Polarization Tests				
Coating	E <sub>corr</sub> (mV <sub>SCE</sub> )	i <sub>corr</sub> (µA/cm <sup>2</sup> )	b <sub>a</sub> (mV/dec)	b <sub>c</sub> (mV/dec)
<b>C</b> 1	= 10	0.40	10	100

couring	Corr SCE	Corr (Print)	a (mittaee)	C (III ) / de
Cd	-740	0.43	19	-139
Zn	-1035	2.20	52	-267
Zn-Ni	-810	0.14	62	-359
Ni-P/Zn	-690	7.90	52	-281

mV. At the beginning of the test the Zn-16.3% Ni alloy samples exhibited a potential below -800 mV. After 20 days, the potential remained constant, near -680 mV. The electroless Ni-6%P/Zn coating showed red rust after 8 days. The corrosion increased and the samples were removed after 21 days. The steel substrate exhibited corrosion and the potential stabilized at about -680 mV.

Figures 4 and 5 show the anodic and cathodic polarization curves. These deposits showed active dissolution in chloride solution. The linear interval shown in the curves was obtained by linear regression which allowed us to determine the corrosion current by straight-line extrapolation to the corrosion potential. The Tafel constants were determined from the slopes. Table 2 shows the results for  $E_{corr}$ ,  $i_{corr}$ ,  $b_a$  and  $b_c$ .

The results of the linear polarization tests are shown in Fig. 6 and Table 3. The coatings, presented in decreasing order of resistance, were: Zn-16.3% Ni alloy (75.8 K $\Omega$ ·cm<sup>2</sup>), cadmium (18.1 K $\Omega$ ·cm<sup>2</sup>), zinc (5.5 K $\Omega$ ·cm<sup>2</sup>) and electroless Ni-6%P/Zn (1.6 K $\Omega$ ·cm<sup>2</sup>). The *B* values calculated from b<sub>a</sub> and b<sub>c</sub> varied between 18.9 and 27.0 mV except for cadmium which was 7.3 mV. The I<sub>corr</sub> values determined from the polarization resistance measurements were close to those found with the anodic polarization tests.

#### Discussion

Metallic coatings applied over a surface for corrosion protection must be continuous, adherent, free of pores and cracks, and chemically inert or remarkably resistant to the work medium. If the coating is more electrochemically active than the substrate, as are cadmium and zinc, it will confer galvanic protection to steel at the beginning of the corrosion process if it exhibits microcracks or microporosity. However, if the coating is nobler than the substrate, like nickel, the presence of defects will soon promote the corrosion of the substrate.

The SEM results revealed that the cadmium and Zn-16.3% Ni alloy coatings were fine-grained and free of defects. By contrast, the zinc coatings showed microcracks across the deposit, while the electroless Ni-6%P/Zn coatings showed microcracks and micropres

Table 3 Results of Linear Polarization Tests				
Coating	$\mathbf{R}_{\mathbf{p}}(\mathbf{K}\Omega\cdot\mathbf{cm}^{2})$	B (mV)	$\mathbf{i}_{\mathrm{corr}}~(\mu\mathrm{A/cm^2})$	
Cd	18.1	7.3	0.4	
Zn	5.5	18.9	3.4	
Zn-Ni	75.8	23.0	0.3	
Ni-P/Zn	1.6	19.1	12.0	



Fig. 5-Cathodic polarization curves of the coatings studied.

on the surface. It is likely that hydrogen under the surface, produced during the electrodeposition and electroless deposition processes, produced the defects. The hydrogen can provoke internal stress, cracks and microfissures in the deposit structure. In the case of the electroless Ni-6%P/Zn coatings, hydrogen relief at 190°C (374°F) for 1 hr and heat treatment at 320°C (608°F) for 1 hr could have easily led to the formation of the many cracks in the deposit surface.

According to Jafar, et al.,13 who studied the corrosion behavior of electroless nickel coatings heat treated at 650°C (1202°F) for 1 hr, the presence of microcracks was the cause of low corrosion resistance. Similar results were found by Kalantary, et al.,14 who detected microcracks in alternating layers of zinc and nickel, occasioning low corrosion resistance. From the point of view of Fujinami and Honma,15 hydrogen was responsible for defects found in copper deposited on ceramic substrates. The presence of cracks produced by hydrogen in Zn-Ni deposits was also observed by Gavrila, et al.,<sup>16</sup> Wright, et al.<sup>17</sup> and Simões, et al..<sup>18</sup>

Salt-spray tests showed that both unscratched cadmium and Zn-16.3% Ni alloy coatings without scratching showed no corrosion after the entire 950 hr test duration. These coatings showed no structural defects. By contrast, the zinc and electroless Ni-6%P/Zn coatings showed poor performance in the salt-spray test probably because of microcracks in the deposit structure.

Corrosion potential measurement by the total immersion method is a simple procedure for evaluating corrosion resistance. In this work, the zinc coating potential remained below -1000 mV over the first 50 days. However, it reached -690 mV after 90 days (Fig. 3) and the specimen showed red rust. At the beginning of the zinc test, the corrosion was primarily found close to the microcracks because of the large potential difference between the coating and substrate (~300 mV). When the substrate started to corrode, the potential increased, trending toward the substrate potential value. Cadmium plated samples did not corrode and the potential remained constant and below that of the substrate potential. According to Gavrila,<sup>16</sup> the potential increase at the beginning of the test for Zn-16.3% Ni alloy coating was associated with dezincification of the alloy. Zaky, et al.,19 studied the microstructure and the corrosion behavior of Zn-5% Ni alloy coatings. They identified a stable  $\gamma$  and a metastable  $\eta$  phase which dissolved rapidly in the corrosive medium. Similar results were found by Krishniyer, et al.,9 who studied Zn-Ni and Zn-Ni-P alloys with a nickel content less than 15%. In our work, the Zn-16.3% Ni alloy coating studied did not corrode and its potential stabilized at -680 mV. The behavior of electroless Ni-6%P/Zn samples was different from the other coatings. The lower potential can be attributed to the enrichment of the surface in the form of a Ni-rich phase by the strong corrosion of zinc promoted by the microcracks. Substrate corrosion appeared on the eighth day when the potential started to decrease.



Fig. 6-Linear polarization curves of the coatings studied.

Anodic polarization tests showed that the coatings studied actively dissolved in chloride solution. The corrosion rate (i\_\_\_) was remarkably low for cadmium (0.43 µA/cm<sup>2</sup>) and Zn-16.3% Ni (0.14  $\mu$ A/cm<sup>2</sup>) but was high for chromated zinc (2.2  $\mu$ A/cm<sup>2</sup>) and electroless Ni-6%P/Zn (7.9  $\mu$ A/cm<sup>2</sup>) coatings. It is known that cadmium coatings show better corrosion behavior than zinc in sea water.5,20,21 It has also been observed that Zn-Ni coatings present a higher corrosion resistance than chromated zinc.6-9,22

The results of the linear polarization tests confirmed that Zn-16.3% Ni alloy showed the best corrosion resistance in 3% NaCl solution, in accordance with the anodic polarization test results. The Zn-Ni coating polarization resistance was about three times better than that of the cadmium coating.

#### Conclusions

The Zn-16.3% Ni chromated alloy showed good corrosion resistance in salt-spray test and in 3% NaCl solution. It was superior to chromated cadmium . The chromated zinc and electroless Ni-6%P/ Zn coatings heat treated at 320°C (608°F) for 1 hr showed microcracks and low corrosion resistance. Corrosion was higher with electroless Ni-6%P/Zn versus zinc because of numerous cracks on the deposit surface.

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