



Study of an alternative phosphate sealer for replacement of hexavalent chromium

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ABSTRACT

This study evaluates the possibility of replacing the hexavalent chromium passivation treatment used as a sealer after phosphating of carbon steel (SAE 1010) by a treatment with niobium ammonium oxalate (Ox). Samples of carbon steel (SAE 1010) after being phosphated in a zinc phosphate bath (PZn + Ni) were immersed in solution of niobium ammonium oxalate (250 mg L⁻¹ of Nb) either at pH 3.0 or pH 8.0. A passivation treatment with a solution with CrO₃ (200 mg L⁻¹ of Cr⁶⁺) was also used for reference. The corrosion resistance of the phosphated samples after passivation treatments was analyzed in a NaCl 0.5 mol L⁻¹ solution using electrochemical impedance spectroscopy (EIS) and anodic polarization curves. Salt spray tests were also performed to evaluate their corrosion resistance. The results showed that the highest corrosion resistance was obtained by passivation in a solution with (250 mg L⁻¹ of Nb) at pH 8.0.

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1. Introduction

Phosphate layers on ferrous and non-ferrous metals improve their surface corrosion resistance by changing their physicochemical properties [1–6]. Despite their use for corrosion protection, phosphate layers by themselves do not produce considerable improvements in the metallic substrate corrosion resistance and need to be used in association with other corrosion protection methods, being used as paint adhesion promoters.

Pre-treatments for painting are often based on phosphating in combination with a sealer to protect the metallic substrate exposed underneath the pores, cracks or defects present in the phosphate layer. Hexavalent chromium, as dichromate or chromate ions [1,6], is the most important sealer used in combination with the phosphating process producing chromium phosphate on the exposed substrate [1]. However, due to its inherent toxicity, the replacement of hexavalent chromium is essential [7].

Passivation treatments with Cr³⁺ have been used as an alternative to Cr⁶⁺. However, trivalent chromium under certain conditions could oxidize to hexavalent chromium and the development of new passivations towards chromium free products is required [7].

Various chromium free alternatives for replacement of hexavalent chromium as a sealer combined with phosphating have been investigated. Acid solutions containing molybdate ions [7], epoxy resin [7], diphenylamine [8], solutions with aluminum and zirconium

[9], polyvinylphenol [10], titanium quelate [11] and fluorine complexes [12] are some examples of alternative sealers. Nevertheless, none of them has so far provided equivalent corrosion resistance to hexavalent chromium as sealers combined with phosphating process [7].

This study evaluates the niobium ammonium oxalate (Ox), [NH₄H₂[(NbO)(C₂O₄)₃].3H₂O], as an alternative sealer for replacement of hexavalent chromium after phosphating of carbon steel.

2. Experimental

2.1. Sample preparation

Plates of carbon steel (SAE 1010) whose composition is shown in Table 1 were used as substrates for the phosphating process. The steel surfaces were prepared for phosphating by grinding with silicon carbide paper successively from #220, #320, #400 and #600. After grinding, the carbon steel samples were exposed to phosphating and passivation/sealing treatments which were carried out according to the following steps [13–15]:

- i. alkaline degreasing at 70 °C for 5 min (a commercial degreasing solution with concentration of 50 g L⁻¹ was used);
- ii. rinsing with water at room temperature;
- iii. accelerating with a titanium phosphate solution (concentration of 3 g/L) at 25 °C for 90 s;
- iv. immersion in the phosphating bath at 25 °C for 5 min;
- v. rinsing with water at room temperature during 1 min;
- vi. passivation/sealing with CrO₃ or NH₄H₂[(NbO)(C₂O₄)₃].3H₂O.

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Table 1

Chemical composition of the carbon steel (SAE 1010) used as metallic substrate for the phosphating process (%m/m).

Elements	C	Si	Mn	P	S	Cr	Ni	Mo
Composition (%m/m)	0.118	0.023	0.310	0.020	0.016	0.024	0.028	0.002

A concentrated phosphating bath was prepared with composition shown in Table 2. From the concentrated solutions, the phosphating baths were prepared by dilution and addition of sodium hydroxide (NaOH 50 wt.%). The phosphating baths were then titrated with 0.1 mol L⁻¹ NaOH solution. The free and total acidity of the phosphating solutions determined by titration and were 1.6 and 28.0 points, respectively. The points correspond to the volumes of NaOH solution used in the titration.

The mass of the phosphate layer and its stabilization time have previously been experimentally determined and are presented in other works [14,15].

2.2. Sealing baths

Two sealing treatments were used. The first was adopted as reference and was carried out by immersion in a solution with chromium trioxide CrO₃ containing 200 mg L⁻¹ of Cr⁶⁺ ions at (35 ± 2) °C. The second was performed using niobium ammonium oxalate (NH₄H₂[(NbO)(C₂O₄)₃],3H₂O) solutions with three different concentrations of niobium, 150, 200 or 250 mg L⁻¹. These solutions were used either at pH 3.0 or pH 8.0 to evaluate the effect of pH on the phosphate coating solubility. The pH was adjusted to 3.0 by diluting the niobium ammonium oxalate solution in deionized water and adjusted to 8.0 by adding a phosphate-buffered solution whose composition is shown in Table 3. Sealing or passivation was carried out by immersion in either of these solutions for 60 s.

2.3. Morphology characterization of the phosphate layer

The morphology of the phosphate layer was observed by Scanning Electron Microscopy (SEM) using a Philips XL30® microscope. The semi-quantitative chemical composition was determined by Energy Dispersive Spectrometer (EDS) in three different areas.

2.4. Electrochemical characterization

A three-electrode set-up cell was used, with an Ag/AgCl and a platinum wire as reference and counter electrodes, respectively. The electrolyte adopted was a NaCl 0.5 mol L⁻¹ solution. Electrochemical impedance spectroscopy (EIS) measurements were carried out using a Gamry EIS 300® frequency response analyzer coupled to a Gamry PCI4/300® potentiostat. All EIS measurements were performed in the potentiostatic mode at the corrosion potential. The amplitude of the perturbation signal was ± 10 mV, and the frequency range investi-

Table 2

Composition of the concentrated phosphate solution.

Composition	(g/L)
H ₃ PO ₄ 85%	521.4
HNO ₃ 33%	363.3
ZnO 99%	160.0
NiCO ₃ 47%	5.0
H ₂ O ₂ 30%	0.032
H ₂ O	434.4
Accelerator(NaNO ₂)	0.5

Table 3

Composition of the phosphate buffered solution used for pH correction.

pH	Composition (V = 1 L)	
	NaOH (0.1 mol L ⁻¹)	KH ₂ PO ₄ (0.1 mol L ⁻¹)
8.0	468.0 mL	500.0 mL

gated was from 100 kHz to 10 mHz with an acquisition rate of 10 points per decade. Anodic polarization measurements were obtained from the corrosion potential up to 400 mV at a scan rate of 1 mV s⁻¹. All electrochemical tests were carried out at (20 ± 2) °C.

2.5. Accelerated corrosion and painting adhesion test

Salt spray tests were performed according to the ASTM B117 standard [16], using a 5 (wt.%) sodium chloride solution. Samples of SAE 1010 carbon steel with 100 mm × 150 mm were painted with white polyester paint, to a thickness of approximately 30 µm. The paint adhesion was evaluated according to NBR 11003/1990 [17]. This test is carried out using a tape pull test in which the amount of paint coating removed by pulling a (32 ± 4) g/mm 3M® tape is determined. The tape was adhered for 1 to 2 min on the scratched area of the phosphate coating and then removed.

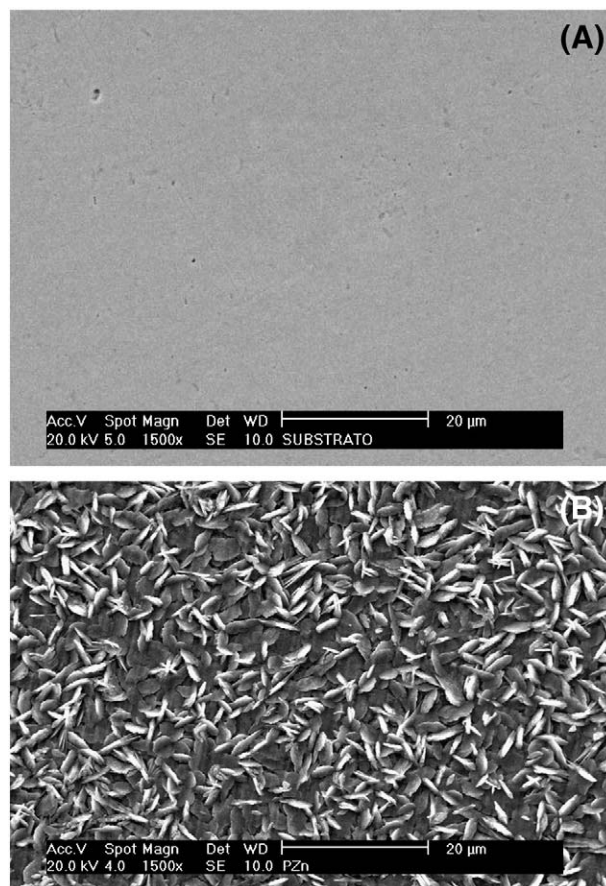


Fig. 1. Micrographs of the carbon steel (SAE 1010) samples (A) as received and (B) PZn + Ni coated (5 min). SEM.

3. Results and discussion

3.1. Morphology and chemical composition of phosphated samples

Fig. 1 shows the SEM micrographs of the as-received carbon steel and zinc phosphate-coated samples showing that the phosphate coating is composed by hexagonal plate crystals of PZn + Ni. The crystals morphology increase the surface roughness and leads to improved paint adhesion [3,18–22]. This morphology is associated to the presence of hopeite, $Zn_3(PO_4)_2 \cdot 4H_2O$ [3,20].

Semi-quantitative chemical analysis of the carbon steel used as substrate and of the phosphate layer was determined by EDS, and the results are presented in Fig. 2 and Table 4.

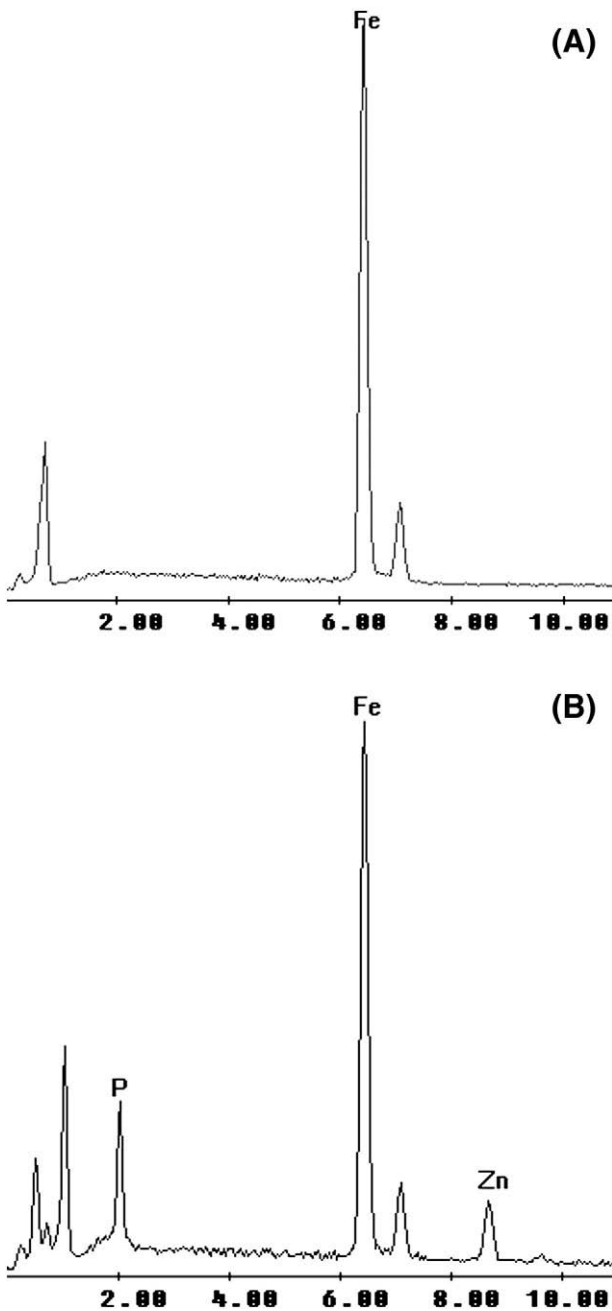


Fig. 2. EDS diagrams of carbon steel (SAE 1010) (A) as received and (B) phosphate coated in a PZn + Ni solution for 5 min. SEM-EDX.

Table 4

Semi-quantitative chemical composition of the phosphate coating analyzed by EDS.

Coating	Chemical composition (wt.%)		
	Zn	Fe	P
PZn + Ni	23.4 ± 2.6	67.7 ± 3.5	8.9 ± 1.2

3.2. Results of samples sealed/passivated in solution at pH = 3.0

EIS diagrams of samples sealed/passivated in a solution with Ox (pH 3.0) were obtained in a NaCl 0.5 mol L⁻¹ solution, and the results are presented in Fig. 3.

The Nyquist diagrams show that the sealing treatment with Ox solutions of pH 3.0 caused the decrease in impedance of the phosphated samples for all concentrations of Nb tested showing that these solutions were not indicated for sealing of the phosphate investigated. On the other hand, sealing/passivating treatment with CrO₃ resulted in higher impedances comparatively to the only phosphated samples, confirming literature results [1,6–12]. It is important to emphasize that the sealing treatment with Ox solution of pH 3.0 is not proper once it leads to the attack of the phosphate layer, as it will be shown later.

Micrographs of unsealed or sealed samples with CrO₃ are shown in Fig. 4. It is clearly seen that sealing with CrO₃ did not promote attack of the phosphate coating. Zn, Fe and P were the only elements detected by EDS analysis. Cr was not detected due to the very thin film formed in the CrO₃ solution. According to the literature, other techniques are necessary to detect the Cr presence in the passive layer formed by the sealing process [23].

Fig. 4B, C and D present micrographs of samples sealed in solutions of pH 3.0 with different concentrations of Nb (Ox). The results suggest that these solutions caused the attack of the phosphate layer, and the solution aggressiveness towards the phosphate film increased with the Nb concentration. Nb was not detected by the EDS analyses due to the too low thickness of the passive film formed in Nb containing solution.

Semi-quantitative chemical composition obtained by EDS analyses of sealed samples is given in Table 5. A comparison of the results of Table 5 with those of Table 4 (phosphated and unsealed samples) shows that sealing in Nb containing solutions leads to decreased amounts of P and Zn in the phosphate layer, whereas passivation in CrO₃ solution seemingly does not attack the conversion layer. This result can be explained by the stronger acidity of the Ox solution comparatively to the Ox one.

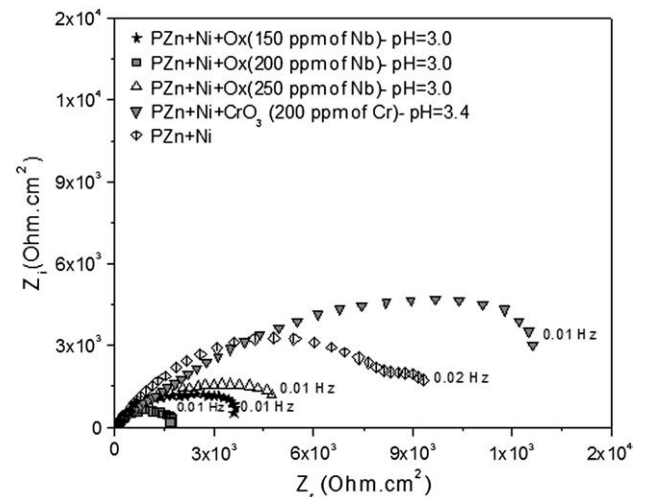


Fig. 3. Nyquist diagrams for the carbon steel PZn + Ni coated and the carbon steel PZn + Ni coated and CrO₃ or Ox sealed, obtained in a NaCl 0.5 mol L⁻¹ solution.

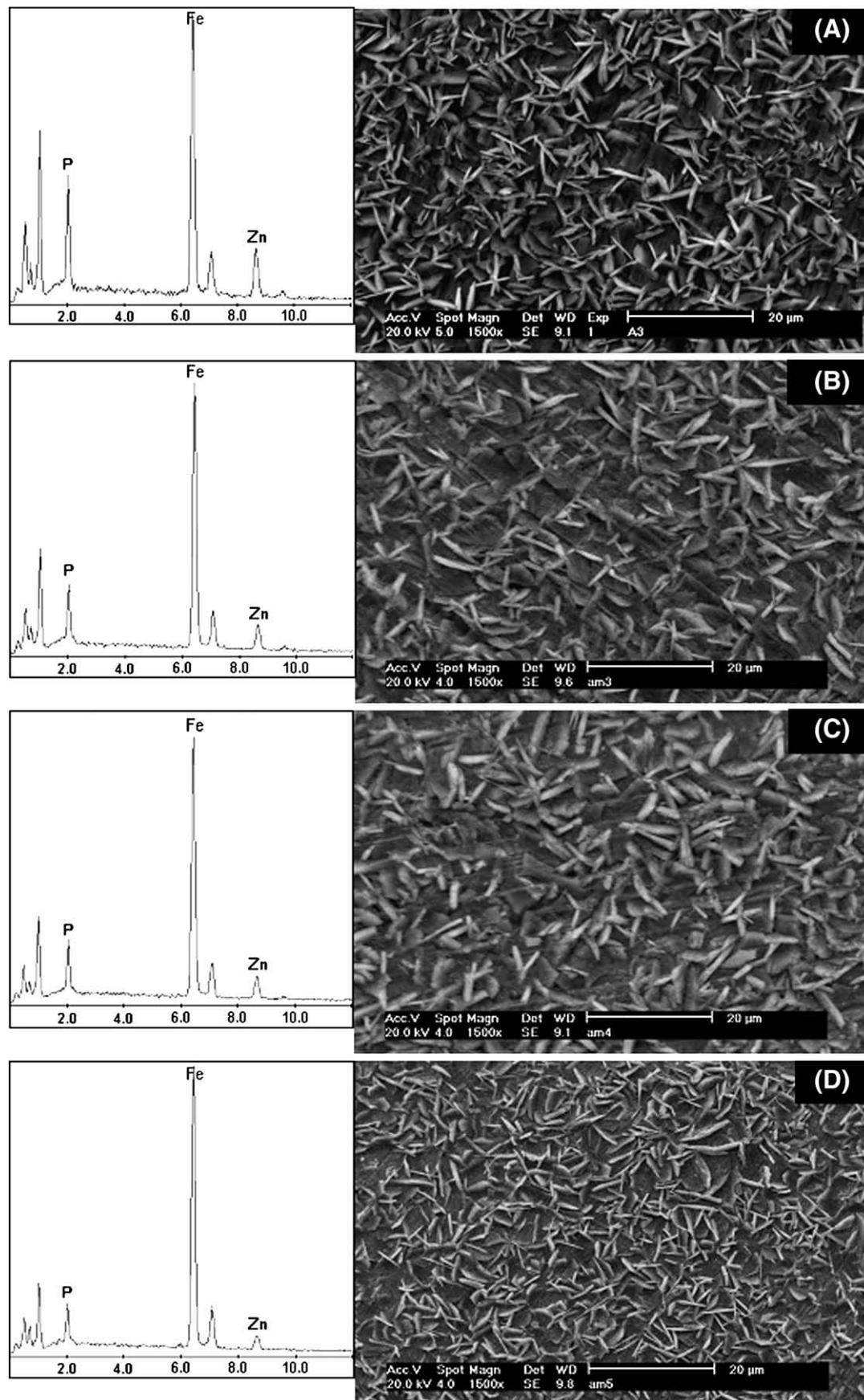


Fig. 4. Micrographs of the carbon steel (SAE 1010) PZn + Ni coated and sealed with (A) 200 mg L⁻¹ of Cr at pH = 3.4, (B) 150 mg L⁻¹ of Nb at pH = 3.0, (C) 200 mg L⁻¹ of Nb at pH = 3.0 and (D) 250 mg L⁻¹ of Nb at pH = 3.0. SEM.

Table 5

Semi-quantitative chemical analyses of the carbon steel (SAE 1010) PZn + Ni coated and CrO₃ or Ox sealed.

Coating	Composition		
	Sealers	Chemical composition (wt. %)	
PZn + Ni	CrO ₃ (200 mg L ⁻¹ of Cr ⁶⁺) pH = 3.4	Zn	22.3 ± 1.3
		Fe	69.2 ± 0.4
		P	8.5 ± 1.6
	NH ₄ H ₂ [(NbO)(C ₂ O ₄) ₃].3H ₂ O–(Ox) (150 mg L ⁻¹ of Nb ⁵⁺) pH = 3.0	Zn	18.4 ± 0.8
		Fe	74.2 ± 0.9
		P	7.3 ± 0.1
	NH ₄ H ₂ [(NbO)(C ₂ O ₄) ₃].3H ₂ O–(Ox) (200 mg L ⁻¹ of Nb ⁵⁺) pH = 3.0	Zn	14.5 ± 3.2
		Fe	80.5 ± 4.3
		P	5.0 ± 1.2
NH ₄ H ₂ [(NbO)(C ₂ O ₄) ₃].3H ₂ O–(Ox) (250 mg L ⁻¹ of Nb ⁵⁺) pH = 3.0	Zn	8.7 ± 2.5	
	Fe	87.9 ± 3.7	
	P	3.4 ± 1.2	

The attack of the phosphate layer sealed in the Ox solutions of pH 3.0 could be the reason for the lower impedances associated to the samples sealed in these solutions comparatively to that passivated in CrO₃ solution. The literature reports [15], that phosphate layers are soluble in pH < 3.0 and pH > 12.0 [24,25]. Accordingly, sealing was carried out in Ox solutions with pH adjusted to 8.0.

3.3. Results of samples sealed/passivated in solution at pH 8.0

Fig. 5 presents micrographs of phosphated samples passivated in Ox solutions at pH 8.0. There is no evidence of corrosive attack of the phosphate layer. The semi-quantitative results of EDS analysis presented in Table 6 show similar amounts of the main elements found in both types of phosphate layers, unsealed or sealed in Ox solutions of pH adjusted to 8.0.

Fig. 6 shows the EIS diagrams of the samples sealed in Ox solutions at pH 8.0 obtained in 0.5 mol L⁻¹ NaCl solution (Fig. 6). The Nyquist

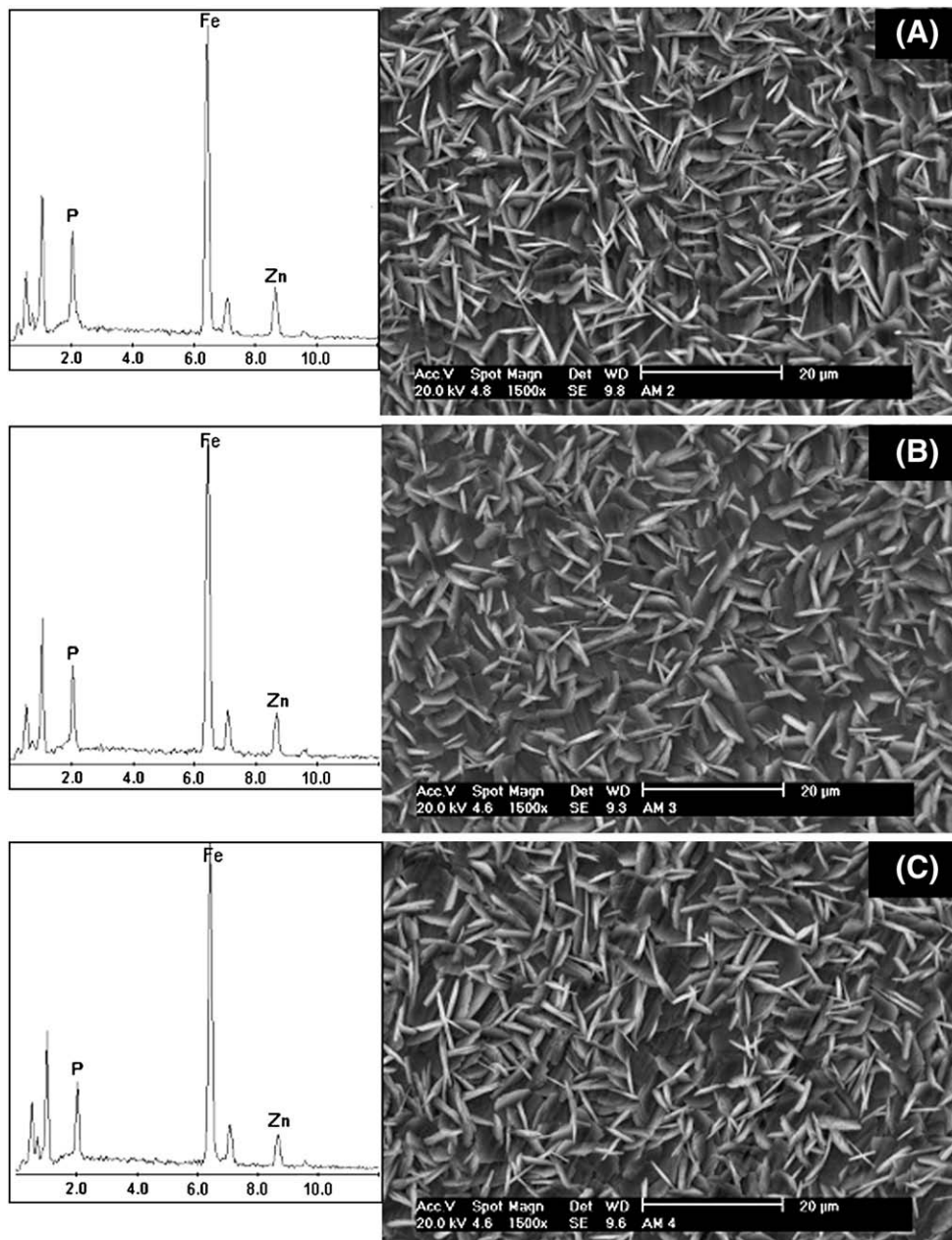


Fig. 5. Micrographs of the carbon steel (SAE 1010) PZn + Ni coated and sealed with (A) 150 mg L⁻¹ of Nb at pH = 8.0, (B) 200 mg L⁻¹ of Nb at pH = 8.0 and (C) 250 mg L⁻¹ of Nb at pH = 8.0. SEM.

Table 6
Semi-quantitative chemical analyses of the carbon steel (SAE 1010) PZn + Ni coated and Ox sealed at pH = 8.0.

Coating	Composition		
	Sealers	Chemical composition (wt. %)	
PZn + Ni	NH ₄ H ₂ [(NbO)(C ₂ O ₄) ₃].3H ₂ O-(Ox) (150 mg L ⁻¹ of Nb ⁵⁺) pH = 8.0	Zn	23.4 ± 2.2
		Fe	70.3 ± 4.0
	NH ₄ H ₂ [(NbO)(C ₂ O ₄) ₃].3H ₂ O-(Ox) (200 mg L ⁻¹ of Nb ⁵⁺) pH = 8.0	P	8.4 ± 0.9
		Zn	23.9 ± 2.6
		Fe	65.3 ± 3.5
NH ₄ H ₂ [(NbO)(C ₂ O ₄) ₃].3H ₂ O-(Ox) (250 mg L ⁻¹ of Nb ⁵⁺) pH = 8.0	P	10.0 ± 1.7	
	Zn	23.7 ± 2.9	
	Fe	67.3 ± 4.0	
		P	8.9 ± 1.0

diagrams show higher impedances associated to the phosphated samples sealed in Ox (PZn + Ni + Ox) compared to those passivated in CrO₃ (PZn + Ni + CrO₃). Sealing had a significant effect on the impedance results suggesting slowing down of the charge transfer processes.

The EIS diagrams of phosphated samples sealed in CrO₃ solution (PZn + Ni + CrO₃) of pH 8.0 showed two time constants as obtained in the similar sealing solution of pH 3.0. The results also showed that sealed samples in Ox with 250 mg L⁻¹ of Nb solution at pH 8.0 presented higher impedances than that sealed in CrO₃, at the same pH. From these results, solutions of Ox with Nb concentrations around 250 mg L⁻¹ of Nb and at pH 8.0 could be considered an alternative for replacement of hexavalent chromium as sealant/passivating combined with phosphating.

3.4. Anodic polarization curves

Anodic polarization curves were obtained for phosphated samples, either unsealed or sealed in the various passivating solutions, and these are presented in Fig. 7. The corrosion rate (*i*_{corr}) values were estimated from the polarization curves for the substrate and for the phosphated steel and the results presented in Table 7. The efficiency of protection (θ) provided by the phosphate layers was also estimated from:

$$\theta = \left[\frac{i_{\text{corr substrate}} - i_{\text{corr phosphate}}}{i_{\text{corr substrate}}} \right] \times 100$$

and the results are also presented in Table 7.

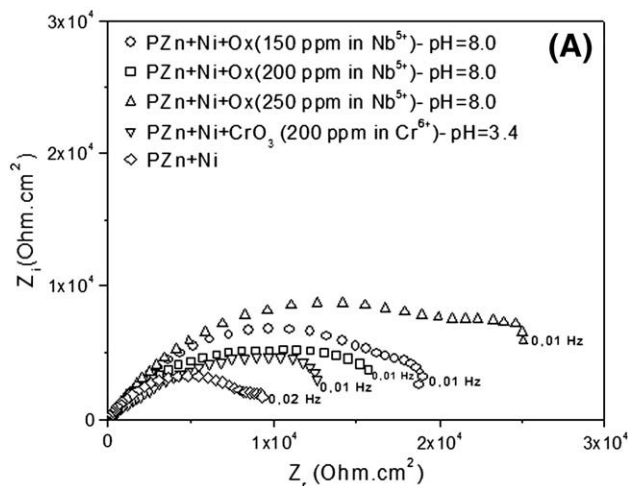


Fig. 6. EIS diagrams for the carbon steel (SAE 1010) phosphate coated with PZn + Ni with and without sealer (A) Nyquist diagram obtained in a NaCl 0.5 mol L⁻¹ solution.

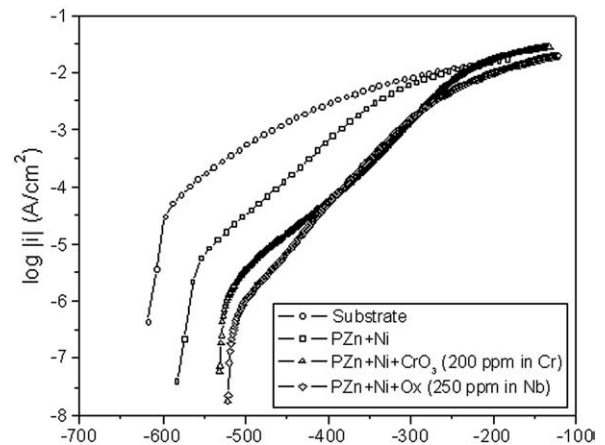


Fig. 7. Anodic potentiodynamic polarization curves in a NaCl 0.5 mol L⁻¹ solution for the carbon steel (SAE 1010) PZn + Ni coated and sealed with CrO₃ or Ox.

The results presented in Table 7 show that the corrosion rates decrease, the corrosion potentials increase and the efficiency of protection provided by the phosphate layers increase in the following order: PZn + Ni, PZn + Ni + CrO₃ and PZn + Ni + Ox.

Sealed samples presented lower current densities than unsealed ones, the lowest currents being associated to the Ox-sealed samples in solution of pH 8.0, confirming the results obtained from EIS.

3.5. Salt spray tests

Salt spray tests were performed according to ASTM B117-90 standard [16] with samples painted with polyester-based white paint Interlac-636 from International Protective Coatings on various types of substrates, specifically, unphosphated carbon steel, phosphated but unsealed, phosphated and CrO₃-sealed, and phosphated and Ox-sealed. Prior to salt spray tests, the organic coating was scratched to expose the substrate. The duration of the salt spray tests was 504 h. This period is determined according to the type of sample, coating and coating process. Automotive paints and varnishes on carbon steel can be exposed for periods between 240 and 480 h. Electrostatically applied powder paints might even be exposed for 3000 h [26].

Fig. 8 show samples exposed to 336 h (14 days) and 504 h (21 days) of salt spray test. Evident signs of intense corrosive attack (Fig. 8A) are associated to the unphosphated and painted samples presented signs of (Fig. 8A). The phosphate-coated samples presented corroded areas after 336 h of salt spray tests. However, the corrosion process occurred only in the areas where the substrate was exposed.

The results obtained confirm the literature data [20,22,26–31]. The paint coatings were evaluated according to their adhesion and their corrosion resistance and the Ox-sealed samples presented the best results.

The adhesion of the paint was tested prior to the salt spray tests, and the results are presented in Fig. 9. The paint applied directly on the

Table 7
Corrosion rates (*i*_{corr}), corrosion potentials (*E*_{corr}) values for the substrate and various types of phosphate layers tested and protection efficiency (θ) values for the layers tested, unsealed and sealed.

Sample	<i>i</i> _{corr} (μA/cm ²)	<i>E</i> _{corr} (V)	θ (%)
Substrate	28.3 ± 3.3	-0.597 ± 0.020	-
PZn + Ni	5.3 ± 1.3	-0.555 ± 0.010	81.3 ± 2.0
PZn + Ni + CrO ₃	1.3 ± 0.9	-0.540 ± 0.030	95.4 ± 1.9
PZn + Ni + Ox	0.8 ± 0.2	-0.525 ± 0.010	97.2 ± 0.4

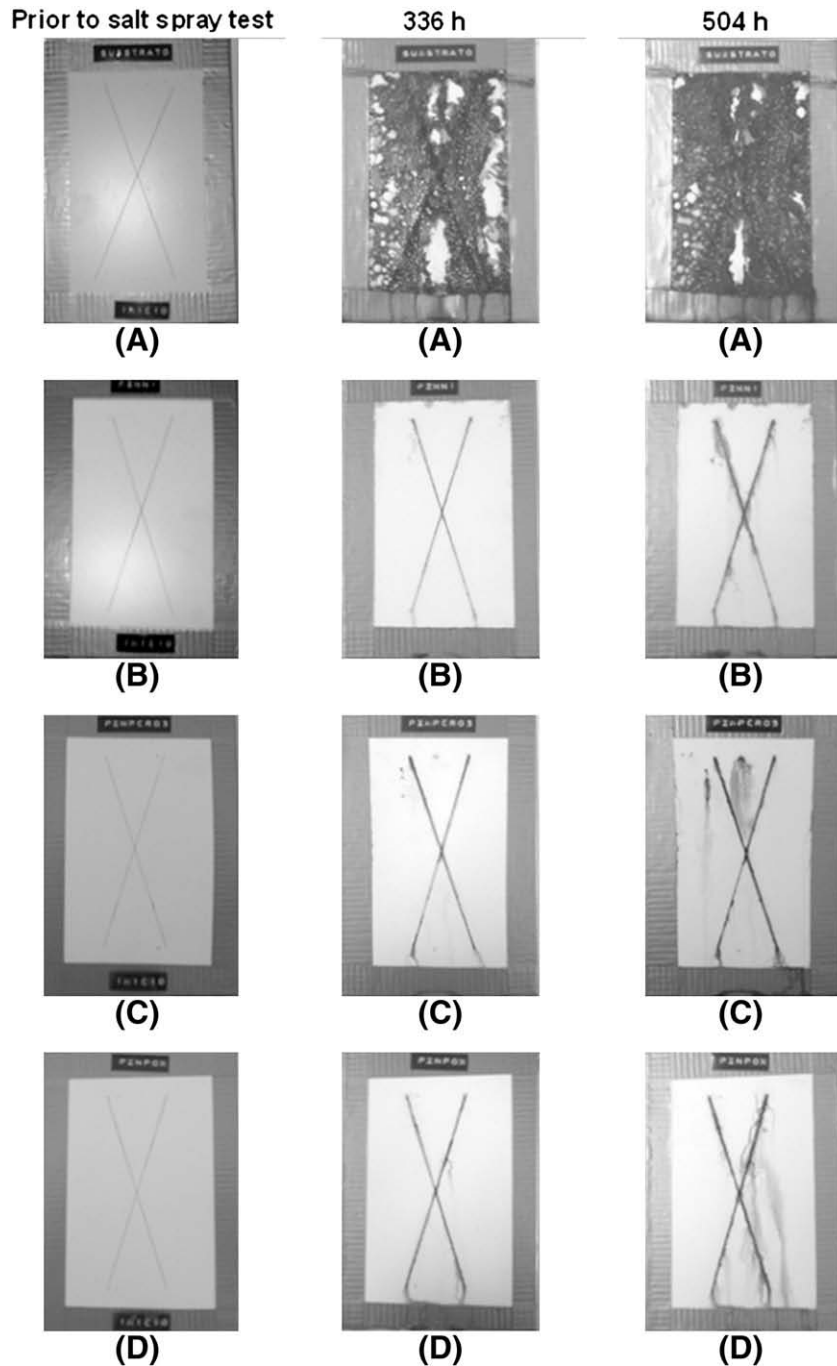


Fig. 8. Macrographs of the carbon steel samples (SAE 1010) (A) painted with Interlac-636, (B) PZn + Ni + Interlac-636, (C) PZn + Ni + CrO₃ + Interlac-636 and (D) PZn + Ni + Ox + Interlac-636 and then painted with polyester-based white paint.

carbon steel presented good adhesion and was not detached, indicating good adhesion characteristics. The adhesion tests performed after 504 h of salt spray tests show that the phosphate layer largely improved the adhesion properties, as shown in Fig. 10. The paint coating was extensively detached from the unphosphated steel substrate (Fig. 10A), however detachment did not occur with the phosphated samples (Fig. 10B). The adhesion of the paint to phosphated and sealed samples was also evaluated. Fig. 10C and D show that sealing with Ox resulted in better adhesion properties than with CrO₃. The salt spray and adhesion tests also supported the electrochemical results, indicating that the Ox is a candidate for replacement of hexavalent chromium as passivating/sealing agent combined with phosphating.

4. Summary

A chromium-free solution composed of niobium and ammonium oxalate at pH adjusted to 8.0 showed passivating/sealing properties of phosphated carbon steel superior to that provided by toxic hexavalent chromium. Besides, sealing/passivating treatment in the Nb containing solution after phosphating led to higher adhesion properties to a polyester based paint compared to passivation with chromium containing solution. These results suggest that the niobium and ammonium oxalate might be a potential candidate for replacement of hexavalent chromium in passivation/sealing treatments.

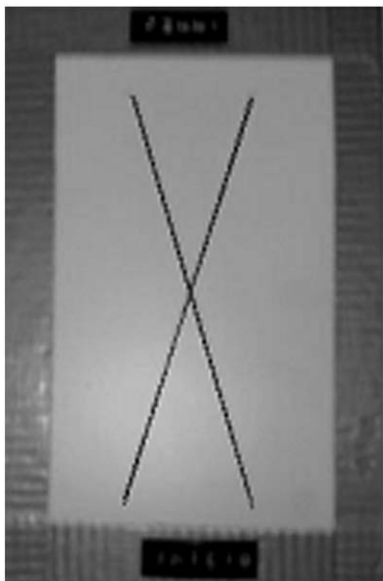


Fig. 9. Carbon steel sample (SAE 1010) PZn + Ni coated after the paint coating adhesion tests.

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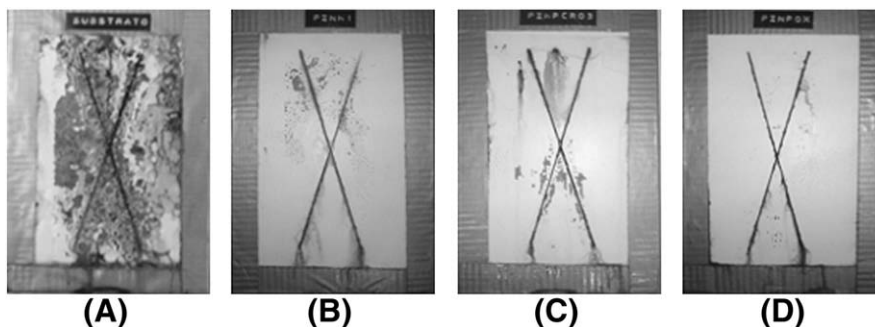


Fig. 10. Macrographs after adhesion tests of the (A) carbon steel samples (SAE 1010), (B) PZn + Ni coated, (C) PZn + Ni + CrO₃ coated, (D) PZn + Ni + Ox coated, painted and salt spray tested for 504 h.