THE EFFECT OF BENZOTRIAZOLE INCORPORTATED IN ZINC PHOSPHATE LAYER AS CORROSION INHIBITOR OF CARBON STEEL

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ABSTRACT

Phosphating and corrosion inhibitors are commonly used for corrosion prevention of metallic materials, mainly carbon steels. In this study, the effect of benzotriazole (BTAH) added to a Zinc phosphating (PZn) bath on the corrosion resistance of a carbon steel (1010) was investigated. Anodic polarization curves and electrochemical impedance spectroscopy (EIS) were used to evaluate the corrosion resistance of the phosphated steel with or without BTAH in 0.5 mol/L NaCl. The results showed better corrosion resistance for the steel phosphated with BTAH comparatively to that without BTAH.

Keywords: Phosphating; inhibitors; benzotriazole; corrosion; carbon steel

INTRODUÇÃO

Phosphating is a conversion coating treatment largely used in many industries as a surface preparation for coating by paints and to increase corrosion resistance (1). Phosphate layer on ferrous or non-ferrous metals(2-6) improve their surface properties by changes in the physico-chemical properties. The main applications of phosphating are for paints adhesion, to increase corrosion resistance, to oil impregnation and to promote electrical insulation (7,8).

Despite of their use for corrosion protection, phosphate layers by themselves do not produce considerable improvements in the metallic substrate corrosion resistance and need to be associated with other corrosion protection methods.

Phosphating processes have been developed for many years, using various additives, such as: nitrites, nitrates, chlorates, hydroxilamines, citric acids, calcium, nickel and manganese(9,10). These additives have are used as accelerators or to improve the properties of the phosphate layers.

The addition of organic compounds to phosphating baths has also been largely reported(9,10). The researches show that these additives cause the improvement in corrosion resistance and decrease the porosity of the phosphate layer (11).

The effect of triazolic compounds as additives for phosphating baths on the corrosion resistance of the metallic substrate was investigated in this study. These compounds are widely used as corrosion inhibitors of various metals in different environments(12-14), mainly for copper and ferrous alloys; among them the most extensively used are benzotriazole BTAH(15-19) and tolytriazole (TTAH)(20). However, the use of these compounds in phosphating baths have hot yet been reported, with the exception of the work of Banczek *et al.*(21). Those authors (21) investigated used TTAH as additive in phosphating baths for carbon steel and found that it caused the increase in the corrosion resistance of the phosphated steel comparatively to that phosphated in a bath without this additive.

The aim of this study was to evaluate the viability of using BTAH as additive in zinc phosphating baths for carbon steel, and to investigate the corrosion resistance of the phosphated substrate in sodium chloride neutral medium (0.5 mol/L NaCl).

MATERIALS AND METODS

Samples preparation

Samples with 60x60x2 mm of carbon steel SAE 1010 containing 0.118% C, 0,023% Si, 0,310% Mn, 0,020% P, 0,016% S, 0,024% Cr, 0,028% Ni, were used as substrate for phosphating.

The surface of the samples were prepared for phosphating by grinding with SiC papers successively from #220, #320, #400 to #600. After grinding, the samples were degreased with commercial alkaline cleaning solution and then rinsed. Subsequently, the samples were immersed in 3 g/L titanium phosphate for 90 seconds at 298 K for surface activation. Next, the samples were immersed in a zinc phosphate PZn bath for 5 minutes, and then dried and weighed, obtaining m_1. For determination of the phosphate deposited mass (m_2), the phosphate coating was solubilized in 5 g/L chromium trioxide solution. The mass of phosphate layer was estimated by equation (A)

$$m_{phosphate} = \frac{m_1 - m_2}{A} \qquad \text{(A)}$$

where m_1 is the mass of the phosphated steel, m_2 is the mass after phosphate layer solubilization, and *A* is the surface area exposed to the phosphating bath.

The chemical composition of the concentrated zinc phosphating bath used in this study is shown in Table 1.

Table 1. Chemical composition of the concentrated phosphating bath used.

Composition of zinc phosphating bath	(%m/m)
H_3PO_4	33
HNO_3	23
ZnO	16
$NiCO_3$	0.5
H_2O_2	0.1
H_2O	27.4

Phosphate layer characterization

The morphology of the phosphate layer was investigated by scanning electron microscopy (SEM) using a Philips XL30 microscope. The electrochemical behaviour of the phosphated samples was analyzed by electrochemical impedance spectroscopy and polarization curves, using a frequency response analyzer (Gamry model EIS 300) coupled to a PCI4/300 potentiostat. Electrodes with 2 cm^2 of geometrical area were used in the electrochemical tests. The electrolyte used for electrochemical characterization it was 0.5 mol/L NaCl solution, at 293 K. All reagents used were p.a. and bidistilled water was used in the electrolyte preparation.

The electrochemical impedance spectroscopy (EIS) tests were carried out potentiostatically at E_{corr}, with voltage perturbation amplitude of 10 mV in the frequency range from 100 kHz to 10 mHz, with an acquisition rate of 10 points per decade.

The potentiodynamic polarization curves were obtained from E_{corr} until -650 mV with a scan rate of 1 $mV.s^{-1}$ in both electrolytes.

RESULTS AND DISCUSSION

Mass of deposited phosphate layer

The average mass of phosphate layer obtained after surface activation in TiO_2 during 90 seconds, in the two phosphating baths, either with (PZn+BTAH) or without PZn additive, and estimated by gravimetric measurements is shown in Table 2.

Table 2. Average mass of phosphate layer obtained in PZn or PZn+BTAH phosphating solutions.

Phosphate layer obtained in	Average mass (g/m^2)
PZn	2.13 ± 0.28
PZn+BTAH	2.48 ± 0.17

The mass of phosphate obtained in PZn+BTAH indicates that a thicker layer was formed in this bath comparatively to that in the PZn one.

Morphological evaluation of phosphate layers.

The Figure 1 shows the morphologies of the steel substrate surface (a) and of the phosphate layer obtained in the two solutions, (b) in PZn and (c) in PZn+BTAH. The energy dispersive spectroscopy (EDS) spectra of the phosphate layers are also presented. This figure shows that the phosphate grains are deposited as hexagonal plates and present a needle-shaped morphology.

The mean size of the needle-shaped crystals obtained in the PZn and PZn+BTAH phosphating baths were (7 ± 3) μm and (4.5 ± 2) μm, respectively. The EDS spectra show that the phosphate layers contain mainly iron, zinc and phosphorus. The high peak of iron is mainly due to the metallic substrate.

The lower crystal sizes obtained in the solution with BTAH indicate that this additive has an effect on surface activation, favouring phosphate nucleation and leading to smaller crystals.

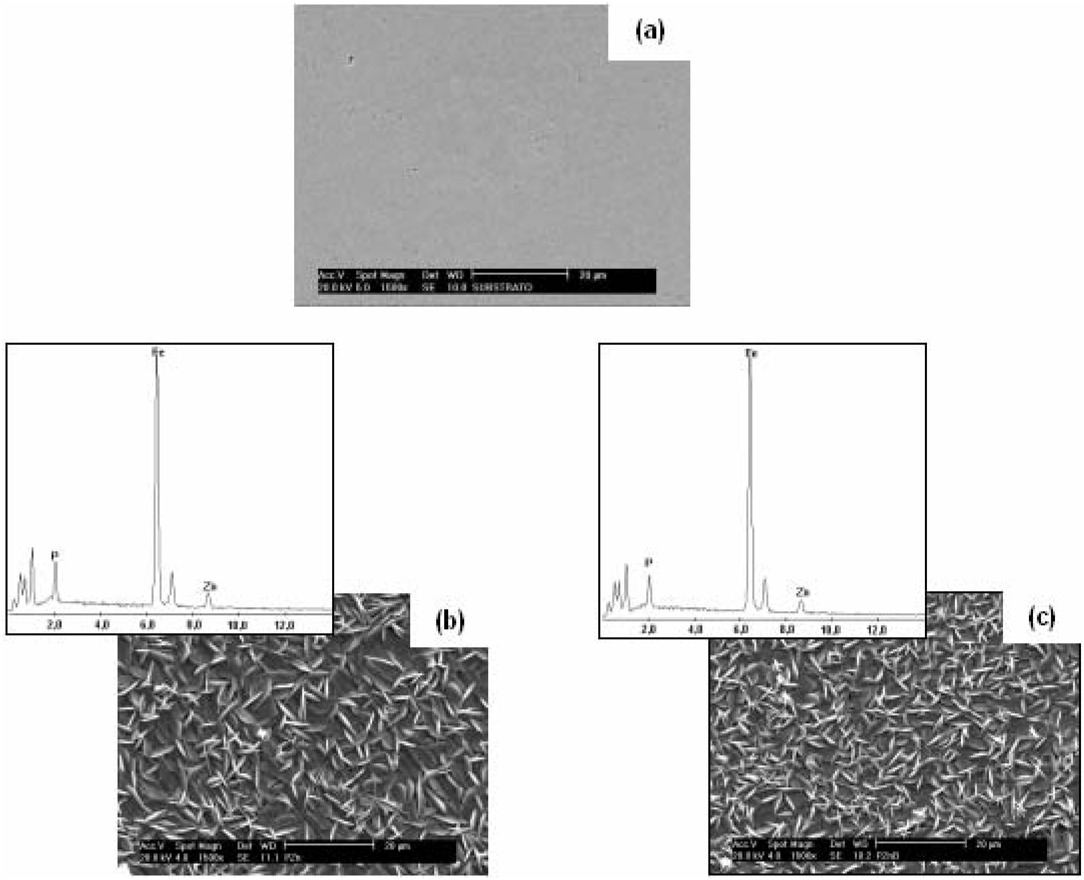


Figure 1. Scanning electron micrographies of (a) SAE 1010 carbon steel, and phosphate layer obtained (b) in PZn, (c) in PZn+BTAH and corresponding EDS spectra.

<u>Electrochemical Characterization</u>

Cathodic polarization curves were obtained in 5 mol/L NaCl solution and the results are shown in Figure 2. A limiting current density (i_L) was obtained for all the samples, phosphated or unphosphated, in this medium, showing a diffusion controlled cathodic process, and the i_L values decreased for the phosphated layers, the smallest values associated to the phosphate layer obtained in PZn+BTAH. This result suggests that the BTAH cause the polarization of the cathodic oxygen reduction reaction.

Corrosion rates (i_{corr}) were estimated by extrapolation of the linear segment of the cathodic curve to the corrosion potential. The average corrosion potential (E_{corr}) and (i_{corr}) values estimated from three measurements and also the corrosion inhibition efficiencies (θ) due to the phosphate layer are shown in Table 3. The results presented in this table show that the phosphate layer moves the E_{corr} into nobler values, suggesting that besides affecting the cathodic reaction it also influences the anodic reaction. It also shows that the efficiency associated to the phosphate layer formed in BTAH containing solution is significantly superior to that of the layer formed in the other solution.

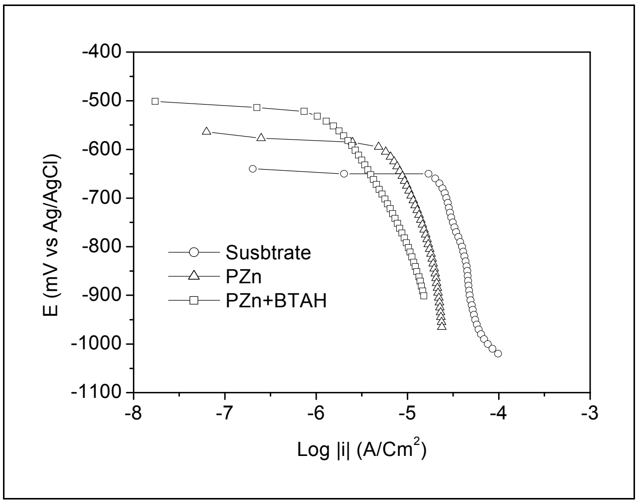


Figure 2. Cathodic polarization curves obtained in 0,5 mol/L NaCl solution for unphosphated and phosphated carbon steel.

Table 3. Average values of i_{corr}, E_{corr} and efficiency (θ) obtained from polarization curves.

Sample	i_{corr}**(μA/cm²)**	E_{corr} **(V)**	**θ (%)**
Substrate	28.3 ± 3.25	-0.597 ± 0.02	-
PZn	5.33 ± 1.32	-0.555 ± 0.09	81± 2.2
PZn+BTAH	1.98 ± 0.29	-0.522 ± 0.02	93 ± 2.5

Figure 3 shows the potentiodynamic anodic polarization curves obtained in 0.5 mol/L NaCl solution. A typical passive behavior is indicated for the phosphated samples at potentials close to E_{corr}, but the breakdown of this layer occurs at potentials of approximately -450 mV and -400 mV, for the phosphated samples obtained in PZn and PZn+BTAH, respectively.

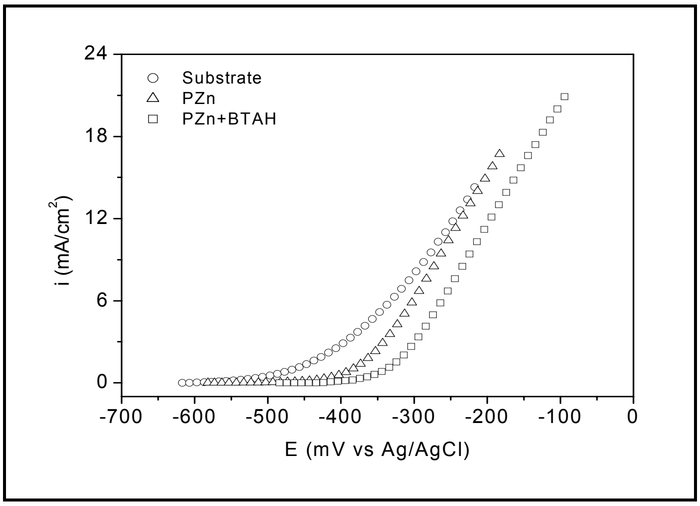
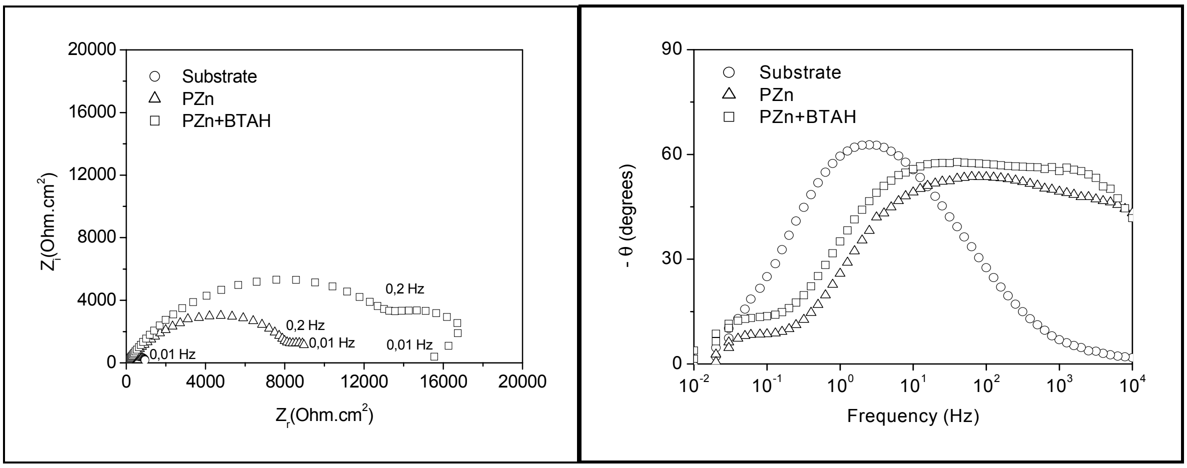


Figure 3. Potentiodynamic anodic polarization curves obtained in 0.5 mol/L NaCl solution for the carbon steel (SAE 1010) unphosphated or phosphate in PZn or PZn+BTAH.

Nyquist and Bode phase angle diagrams for the various tested samples in 0.5 mol/L NaCl electrolyte are shown in Figure 4. The Nyquist diagrams (Figure 4 (A)), show for the phosphated samples two flattened capacitive semicircles and the Bode diagrams (Figure 4 (B)) for the same samples show a large phase angle peak from high frequencies until approximately 10 Hz, suggesting the interaction of more than one time constant and at low frequencies another small peak. For the unphosphated substrate only a time constant is indicated by a peak at frequencies around 1 Hz.



(a) (b)

Figure 4. (a) Nyquist and (b) Bode phase angle diagrams obtained after 2 h of immersion in 0.5 mol/L NaCl solution, for unphosphated or phosphated carbon steel in PZn or PZn+BTAH.

The large peak at high frequencies and at phase angles lower than 60 degrees is associated to the porous phosphate layer on the metallic substrate. The interaction of various time constants results in the very flattened semicircle obtained. The time constant at low frequencies is likely due to the corrosive attack of the exposed substrate. The Nyquist diagrams clearly show the beneficial effect of the phosphate layer on the corrosion resistance of the 1010 carbon steel, causing a large increase in the impedance of the substrate, mainly that obtained in PZn+BTAH phosphating bath, supporting the previous presented results.

The surface of the various tested samples were observed by SEM and analysed EDS for a immersion period of 2 hours in 0.5 mol/L NaCl solution and the corresponding micrographies and EDS spectra are shown in Figure 5.

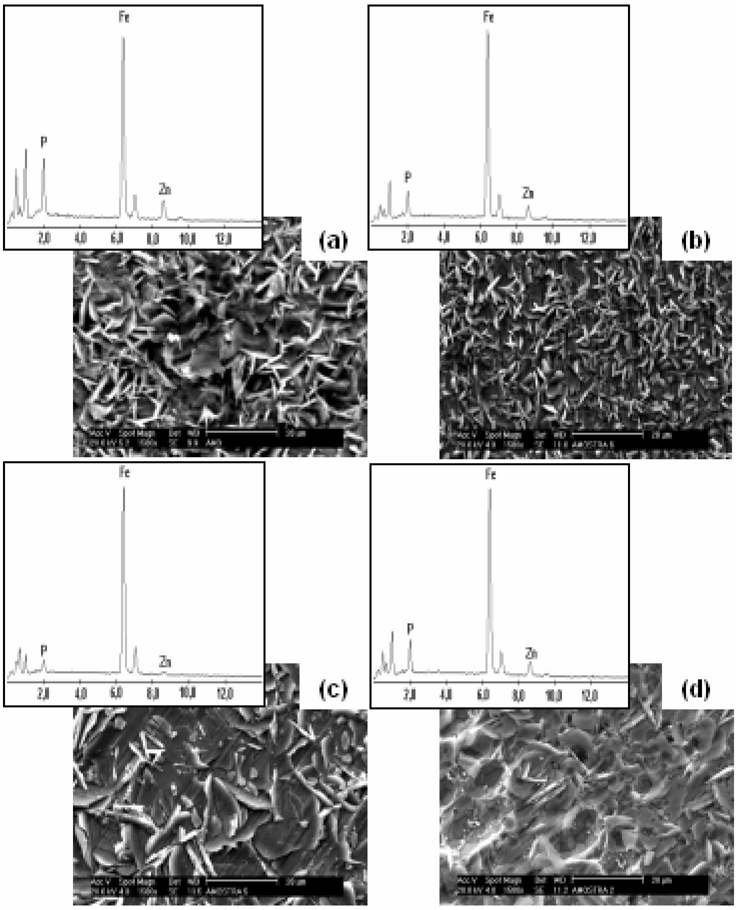


Figure 5. Micrographies and EDS spectra of phosphated samples after 2 h of immersion in 0.5 mol/L NaCl solution. Phosphate obtained in (a) (PZn) and (b) (PZn+BTAH) baths, previous to polarization, and obtained in (c) (PZn) and (d) (PZn+BTAH) baths, after polarization.

In the sodium chloride medium after 2 hours of immersion only localized attack was observed on the phosphated samples, mainly on the layer formed in PZn comparatively to that in PZn+BTAH.

The surface of the phosphated samples were also observed by SEM and analysed by EDS after polarization tests (Figure 5 (c) and (d)) and the results showed that only partial removal of the phosphate layer occurred during polarization, and that the layer formed in PZn+BTAH was more resistant to the corrosive attack.

The results indicate that the resistance of the phosphate layer to corrosive attack in the neutral chloride medium causes a large increase in the substrate corrosion resistance and that the incorporation of BTAH into the phosphating bath has a high beneficial effect to the corrosion properties of the obtained layer.

CONCLUSIONS

In the sodium chloride neutral medium (0.5 mol/L NaCl) the phosphate layers obtained in the PZn and PZn+BTAH solutions showed high corrosion resistance, and the layer obtained in PZn+BTAH was significantly more resistant than that in PZn. The BTAH additive apparently favors phosphate nucleation resulting in particles of lower size and also in a more compact layer of higher weight than that formed in PZn, increasing the corrosion resistance of the metallic substrate.

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