

A comparison between the titanium-based and the zinc phosphate dispersion conditionings of zinc phosphate baths

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RESUMO

A fosfatização é um tratamento de superfícies metálicas muito utilizado no meio industrial pois proporciona maior aderência do filme de tinta ao substrato metálico e maior eficiência na inibição da corrosão. Os agentes condicionantes no processo de fosfatização contribuem para a redução do tempo de obtenção da camada de fosfato e favorecem o refinamento dos cristais formados. Comercialmente, o agente condicionante mais utilizado é a base de sais de titânio, no entanto, é possível que outros compostos, possam ser uma alternativa na otimização do processo industrial. Portanto, com o intuito de reduzir o tempo e a temperatura do processo de fosfatização, esse trabalho tem por objetivo verificar o desempenho do uso do agente condicionante a base de fosfato de zinco na obtenção da camada fosfatizada, quanto à resistência à corrosão, em comparação ao condicionador à base de titânio. Para tanto, amostras de aço carbono SAE 1010 foram desengraxadas e jateadas, imersas por 1 minuto na solução condicionante (titânio ou fosfato de zinco) e fosfatizadas com solução comercial de fosfato de zinco tricatiónico em diferentes temperaturas (40 e 50°C) e tempos de imersão (2, 3 e 4 minutos). As massas depositadas dos revestimentos de fosfato foram medidas e os revestimentos caracterizados por microscopia eletrônica de varredura (MEV), por meio de ensaios eletroquímicos de potencial de circuito aberto e polarização potenciodinâmica. Os resultados mostraram que a maior cobertura do substrato, com a formação de camadas mais densas melhora o desempenho anticorrosivo das amostras fosfatizadas com ambos condicionadores. Para o condicionador a base de titânio, as condições ótimas de fosfatização foram de 3 min a 50°C, enquanto para o condicionador de fosfato de zinco, foram de 2 min a 40°C. Portanto, indica-se para uso comercial a imersão em condicionador a base de fosfato de zinco, seguido de fosfatização por 2 min a 40°C.

Palavras-chave: Fosfatização; SAE 1010; Agente condicionante; Corrosão.

ABSTRACT

Phosphating is a metallic surface treatment widely used in the industrial environment as it provides greater adhesion of the paint film to the metallic substrate and greater efficiency in inhibiting corrosion. The conditioning agents in the phosphating process contribute to reducing the time to obtain the phosphate layer and favor the refinement of the formed crystals. Commercially, the most used conditioning agent is based on titanium salts, however, it is possible that other compounds may be an alternative in optimizing the industrial process. Therefore, with the aim of reducing the time and temperature of the phosphating process, this work aims to verify the performance of using the conditioning agent based on zinc phosphate in obtaining the phosphatized layer, in terms of corrosion resistance, in comparison with to the titanium-based conditioner. For this purpose, SAE 1010 carbon steel samples were degreased and sandblasted, immersed for 1 minute in the conditioning solution (titanium or zinc phosphate) and phosphated with a commercial solution of tricationic zinc phosphate at different temperatures (40 and 50°C) and immersion times (2, 3 and 4 minutes). The deposited masses of the phosphate coatings were measured and the coatings characterized by scanning electron microscopy (SEM), through electrochemical tests of open circuit potential and potentiodynamic polarization. The results showed that the greater coverage of the substrate, with the formation of denser layers, improves the anticorrosive performance of samples phosphated with both conditioners. For the titanium-based conditioner, the optimal phosphating conditions were 3 min at 50°C, while for the zinc phosphate conditioner, they were 2 min at 40°C. Therefore,

for commercial use, immersion in a zinc phosphate-based conditioner is indicated, followed by phosphating for 2 min at 40°C.

Keywords: Phosphating; SAE 1010; Conditioning agent; Corrosion.

1. INTRODUCTION

The durability requirements of metallic components, especially by the automotive industry, have leveraged research in order to improve or develop new surface treatments that minimize corrosion losses [1–4]. In order to reduce these losses, corrosion protection techniques, such as phosphating, have been improved and/or developed over the years [5].

Phosphating is widely used in industry as a pre-treatment of metallic surfaces to receive painting processes, as in addition to promoting better adhesion of the paint to the substrate, it contributes to increased resistance to corrosion by creating a barrier against oxygen and humidity [6–10]. It is a fundamental step in the painting processes of automotive components, being required by large automakers [11].

The phosphating process consists of depositing a layer of phosphate on the metallic surface, and phosphating baths based on zinc phosphate use conditioning agents as a stage that immediately precedes phosphating, especially when alkaline degreasing or acid pickling stages are employed [12, 13].

The most commercially used conditioning agent is formulated based on titanium salts, but other compounds, according to the literature, have a similar effect in obtaining phosphated layers, such as: oxalic acid, amine soaps or finely ground zinc phosphates [14, 15]. Despite the widespread use of titanium-based conditioners, these products, when in solution, have a low shelf life and their performance is compromised by factors such as pH, water hardness and temperature [16, 17]. The frequency of changing these conditioning baths is weekly, in most processes, which entails the consumption of water and chemical products, in addition to the treatment of the effluent generated.

An available alternative to titanium-based conditioners is the use of zinc phosphate dispersion as a conditioning agent. Zinc phosphate conditioning baths, according to the manufacturer (for reasons of industrial secrecy, the name of the manufacturer will not be informed), promote a reduction in the time of formation of the phosphate layer and in the phosphatization temperature, resulting in gains in the production process. In this sense, the objective of the present work is to verify the performance of the use of zinc phosphate conditioner in obtaining the phosphate layer in terms of corrosion resistance compared to the titanium-based conditioner. It should be noted that the novelty of this work is the fact that zinc phosphate is not usually used for this purpose, despite the literature citing it as an alternative. There are no reports in the literature describing the phosphating process using zinc phosphate, only titanium-based.

2. METHODOLOGY

2.1. Materials and chemical reagents

The test specimens were made of SAE 1010 carbon steel, measuring 100 × 150 × 0.6mm. These were cut with goldsmith's saws, in order not to damage the phosphate layer during cutting. From these specimens, after phosphating, smaller specimens were cut according to the test to be carried out. The reagents used in the analysis of process parameters are analytical grade. The solutions used for the treatment of samples by the phosphatization process are commercial grade and for reasons of secrecy the supplier of these products and their formulation will not be disclosed. However, to obtain the reproducibility and reliability of this work, it is sufficient to use any commercially available phosphating, titanium conditioner, zinc and passivator solutions that are similar to the chemical compositions indicated in the FISPQ's (Information Sheet of Chemical Product Safety) used in this work. In the preparation of the baths, deionized water (DI) was used.

2.2. Sample surface preparation

The blasting of the SAE 1010 steel samples was done with glass microspheres, after degreasing the surface, in a suction cabinet, model GS 9075-X, CMV brand, with the jet pressure set at 4 bar. The roughness after the blasting process was $R_a = 1.6308 \mu\text{m}$ and $R_z = 11.3293 \mu\text{m}$.

The phosphating process of the samples was carried out on a laboratory scale, in solutions with a volume of 5 L, by immersion, performed in triplicate according to the steps of degreasing, surface conditioning, phosphating and passivation, described below:

- Surface degreasing: the blasted specimen was immersed in a commercial alkaline degreasing solution, concentration 6% v/v, based on potassium hydroxide, for 5 minutes ($60 \pm 5^\circ\text{C}$), rinsed in running water, dried in an oven for 10 minutes at 80°C and finally its mass was measured.

- Surface conditioning: two conditioning solutions were prepared, with a concentration of 1g/L, one based on titanium and the other based on zinc phosphate. Phosphate specimens of each of the conditioners were produced. The immersion time in the conditioning solution was 1 minute, without subsequent rinsing, as recommended by the manufacturer, and the sample was immediately phosphated. The formulation of each of the conditioners used is described in Tables 1 and 2. The values of 30–60% are the composition of the product supplied by the manufacturer and described in the FISPOQ.
- Phosphating: samples were immersed in a commercial tricationic zinc phosphate solution. The phosphating solution was prepared with a concentration of 2.73% by volume, 0.06% accelerator and the volume completed with water. Phosphating was performed at different temperatures (40 and 50°C) and times (2, 3 and 4 minutes) of immersion. After phosphating, the samples were rinsed with DI water. The commercial phosphating solution is formulated as described in Table 3. The accelerator used is based on sodium nitrite and the recommended accelerator concentration should be around 1.5–2.8 mL based on the reading on the saccharometer, that is, it is the volume of accelerator necessary to react with the sulfamic acid and release the amount of 1.5 to 2.8 mL of gas on the saccharometer scale.
- Passivation: the samples were immersed in the passivation solution for 1 minute, rinsed in DI water, and dried in an oven at 80°C/10 minutes. The mass of the samples was again measured on an analytical balance, and the difference between the mass before and after phosphating is the mass of the phosphate coating. The passivation solution was assembled with a concentration of 1% by volume, from a commercial solution based on triethanolamine and nitric acid.

The concentrations of the solutions used in the phosphating process were analyzed according to the methodology described in the technical bulletin of each product and adjusted to meet the specified work ranges. Likewise, the temperature and immersion time parameters used in this work are in accordance with the range recommended by the manufacturer. The heating of the degreasing and phosphating solutions was carried out using a heating plate, Fisaton brand. Temperature control was performed with a digital thermometer ranging from 0 to 250°C. To help understanding the results obtained and the phosphating process carried out, the samples were named according to Table 4. All samples were carried out in triplicate to ensure reproducibility.

Table 4 describes the nomenclature of the samples used in this work, in which Ti or Zn is related to the type of conditioner used, titanium or zinc, 2, 3 or 4, to the time of immersion in the phosphating solution and 40 or 50, to the temperature employed during phosphating.

Table 1: Chemical composition of titanium based conditioner.

CHEMICAL REAGENT	COMPOSITION (% BY MASS)
Triphosphoric acid, pentasodium salt	30–60
Tetrasodium pyrophosphate	1-2
Dipotassium Hexafluorotitanate	1-2

Table 2: Chemical composition of zinc phosphate-based conditioner.

CHEMICAL REAGENT	COMPOSITION (% BY MASS)
Bis (orthophosphate) trizinc Trizinc	30–60

Table 3: Chemical composition of commercial phosphating solution.

CHEMICAL REAGENT	COMPOSITION (% BY MASS)
Bis(dihydrogenphosphate) zinc	15–20
Bis(dihydrogenphosphate) manganese	10–12.5
Bis(dihydrogenphosphate) nickel	3–5
Phosphoric acid	10–12.5
Zinc nitrate	2–3

Table 4: Nomenclature of steel samples phosphated using titanium and zinc conditioners.

SAMPLE	TYPE OF CONDITIONER	PHOSPHATE IMMERSION TIME (MINUTES)	PHOSPHATING SOLUTION TEMPERATURE (°C)
Ti-2-40	Based on Titanium	2	40
Ti-3-40	Based on Titanium	3	40
Ti-4-40	Based on Titanium	4	40
Ti-2-50	Based on Titanium	2	50
Ti-3-50	Based on Titanium	3	50
Ti-4-50	Based on Titanium	4	50
Zn-2-40	Based on Zinc	2	40
Zn-3-40	Based on Zinc	3	40
Zn-4-40	Based on Zinc	4	40
Zn-2-50	Based on Zinc	2	50
Zn-3-50	Based on Zinc	3	50
Zn-4-50	Based on Zinc	4	50

2.3. Characterization of samples

To determine the deposited mass of phosphate, an analytical scale with a capacity of 220 g, Shimadzu brand, model ATX 224, was used. The layer mass was calculated in g/m^2 , using equation (1):

$$Phosphate\ mass\left(\frac{g}{m^2}\right) = \frac{(M1 - M2)}{A} \quad (1)$$

M1 = mass of the phosphated sample, in grams; M2 = mass of the sample after blasting and degreasing, in grams; A = total area of the specimen, in m^2 ;

For SEM analyses, 1 cm^2 specimens were used, metallized with a gold target for electrical conduction and image acquisition. After metallization, the samples were analyzed in top view. The SEM equipment used for analysis has a Jeol model JSM-6510LV.

The electrochemical tests were carried out in a potentiostat model PGSTAT 302 equipment, AU-TOLAB brand. A platinum wire was used as a counter electrode (2.2 cm^2) and saturated calomel (ECS) as a reference electrode. SAE 1010 steel samples, without and with previous conditioning of the surface with conditioning agent based on titanium or zinc (immersed for 1 minute in the conditioning solution) at different times and temperatures were used as working electrode. The open circuit potential of the samples was evaluated to follow its variation with the time of exposure to the commercial solution of tricationic zinc phosphate, at a temperature of 50°C, for 600s. For measurements of potentiodynamic polarization, samples were evaluated in 0.01 M NaCl electrolyte, simulating a corrosive atmosphere. This analysis was initiated at -200mV to 400mV with respect to the open circuit potential. The sweep was 10 mV/dec and the speed was 1 mV/s. The assays were carried out in triplicate.

3. RESULTS AND DISCUSSION

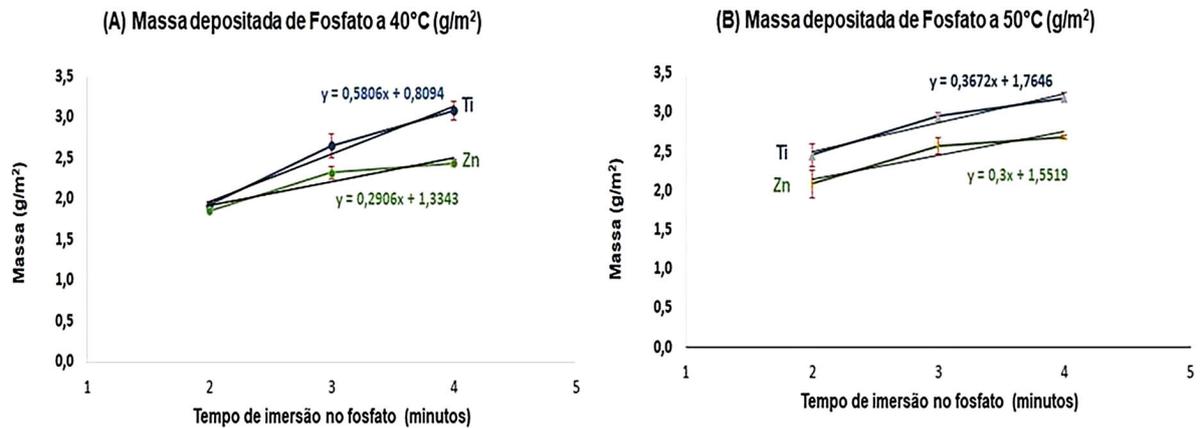
3.1. Determination of phosphate masses deposited per unit area

Table 5 shows the results of the average mass of the phosphate coatings obtained at different temperatures, immersion times and surface conditioning.

It is also observed, according to Figure 1, that the deposited mass increases with the immersion time in the phosphating solution. According to JIANG *et al.* [18], increasing the immersion time influences the deposited mass, until there is a balance between the electrochemical dissolution of the substrate and the formation of crystals. The manufacturer of the phosphating solution used states that its product produces layers of phosphate after 2 to 4 minutes of immersion, which is why this time range was used. Complete phosphating only occurs when this equilibrium is established, with shorter times determining the obtaining of incomplete layers, and longer times, an increase in the size of the formed crystals or the dissolution of the layer. Therefore, the increase in the masses of the phosphated layers with the immersion time at the two temperatures used, using the zinc and titanium conditioners, may be related to the nucleation of the surface and the formation of crystals.

Table 5: Average mass of phosphate coatings obtained at different temperatures, immersion times and surface conditioning (g/m²).

SAMPLE	AVERAGE (g/m ²)
Ti-2-40	1.92 ± 0.05
Ti-3-40	2.65 ± 0.14
Ti-4-40	3.08 ± 0.12
Ti-2-50	2.46 ± 0.14
Ti-3-50	2.95 ± 0.04
Ti-4-50	3.19 ± 0.07
Zn-2-40	1.86 ± 0.03
Zn-3-40	2.32 ± 0.07
Zn-4-40	2.44 ± 0.04
Zn-2-50	2.09 ± 0.18
Zn-3-50	2.57 ± 0.10
Zn-4-50	2.69 ± 0.03


Figure 1: Shows the comparison of the average masses obtained in the samples phosphated in triplicate, from the titanium and zinc conditioners, at temperatures of 40°C and 50°C.

The gravimetric curves for both evaluated conditioners demonstrate that with the increase in temperature from 40 to 50°C, a greater deposit of phosphate occurs on the metallic substrate. These results are possibly related to the increase in the equilibrium constant of the phosphatization reaction, which is favored by temperature. The greater the equilibrium constant, the greater the formation of insoluble phosphates that make up the phosphate layer. LIMA *et al.* [19] obtained layers with higher zinc phosphate deposits and better corrosion protection properties when using temperatures of 50 and 60°C compared to a temperature of 40°C.

3.2. Morphological analysis obtained by SEM of the influence of the phosphating time at a temperature of 40°C

Figure 2 shows the SEM micrographs obtained from the top after 2, 3 and 4 minutes of immersion in the phosphating solution at 40°C, using the titanium conditioner, at magnifications of 500 and 1,000×.

In samples previously conditioned with titanium salts, Figure 2, it is observed that Ti-2-40 and Ti-3-40 present regions that were not covered by phosphate crystals, as exemplified by the outlines in yellow. The Ti-4-40 sample, despite showing greater crystal nucleation and a smaller uncoated area in relation to times of 2 (Ti-2-40) and 3 minutes (Ti-3-40), did not show total substrate coverage. This indicates that the immersion times in the phosphating solution were not sufficient for the complete formation of the phosphate coating. It is observed that the increase in time favors the number of cores, resulting in greater deposit of the coating. However, apparently the size of the nuclei remains the same, not being influenced by time.

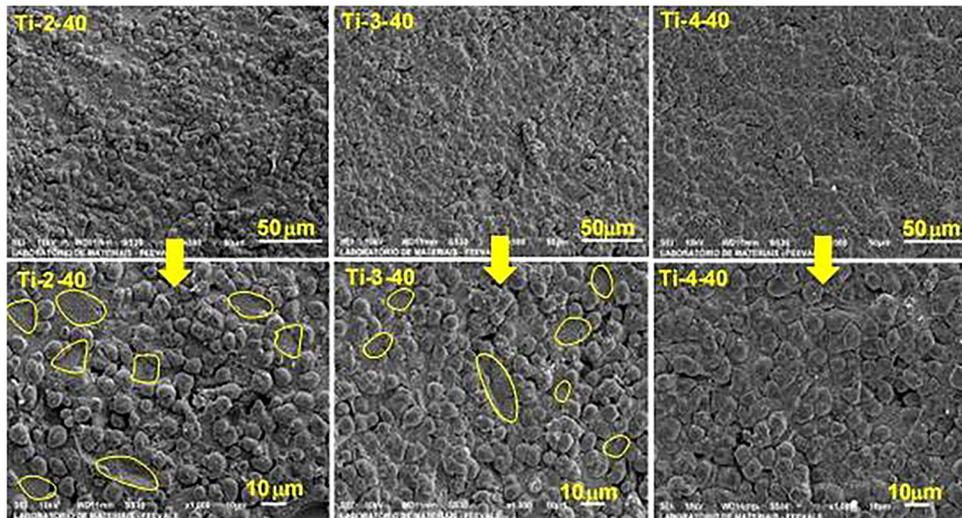


Figure 2: Top view micrographs obtained using the titanium-based conditioner, with 2, 3 and 4 minutes of immersion in the phosphating solution at 40°C at different magnifications.

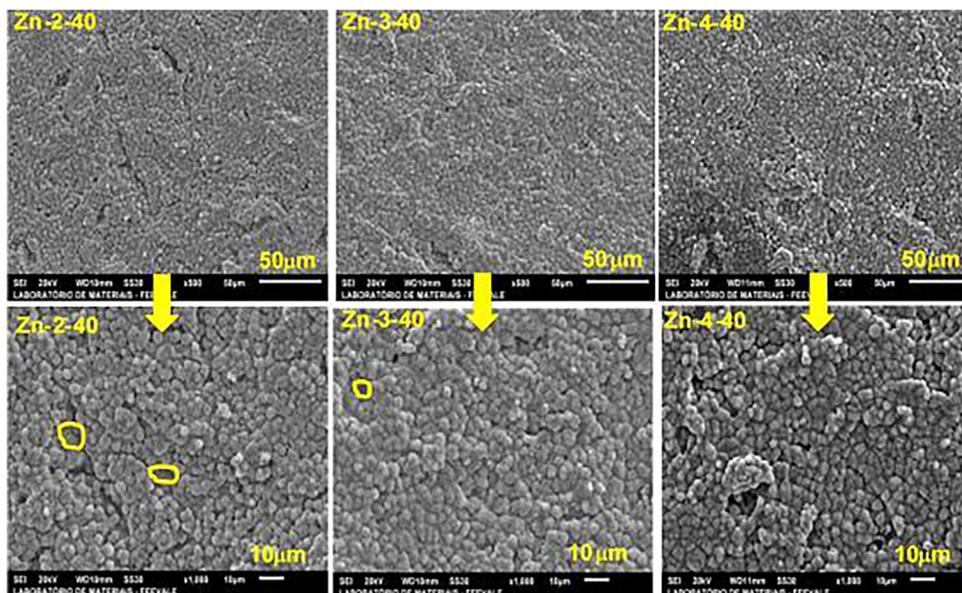


Figure 3: Micrographs in top view obtained using the zinc phosphate-based conditioner, with 2, 3 and 4 minutes of immersion in the phosphating solution at 40°C in different magnifications.

Figure 3 shows the top micrographs obtained after 2, 3 and 4 minutes of immersion in the phosphating solution at 40°C, using the zinc phosphate conditioner, at magnifications of 500 and 1,000×.

In the samples etched with zinc phosphate (Figure 3) the formation of phosphate crystals is observed at all times evaluated, and the Zn-2-40 and Zn-3-40 samples show small areas of the substrate without phosphate coating, exemplified with yellow outlines. In the immersion time of 4 minutes, the formation of a dense and homogeneous layer is verified.

3.3. Morphological analysis obtained by SEM of the influence of the phosphating time at a temperature of 50°C

Figure 4 presents the top micrographs obtained after 2, 3 and 4 minutes of immersion in the phosphating solution at 50°C, using the titanium conditioner, at magnifications of 500 and 1,000×.

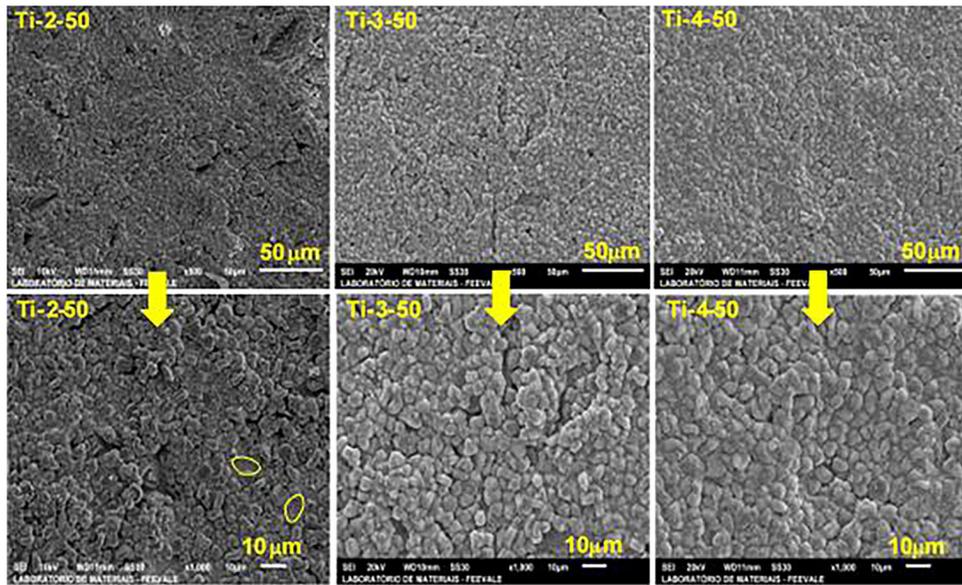


Figure 4: Micrographs in top view obtained using the titanium-based conditioner, with 2, 3 and 4 minutes of immersion in the phosphating solution at 50°C.

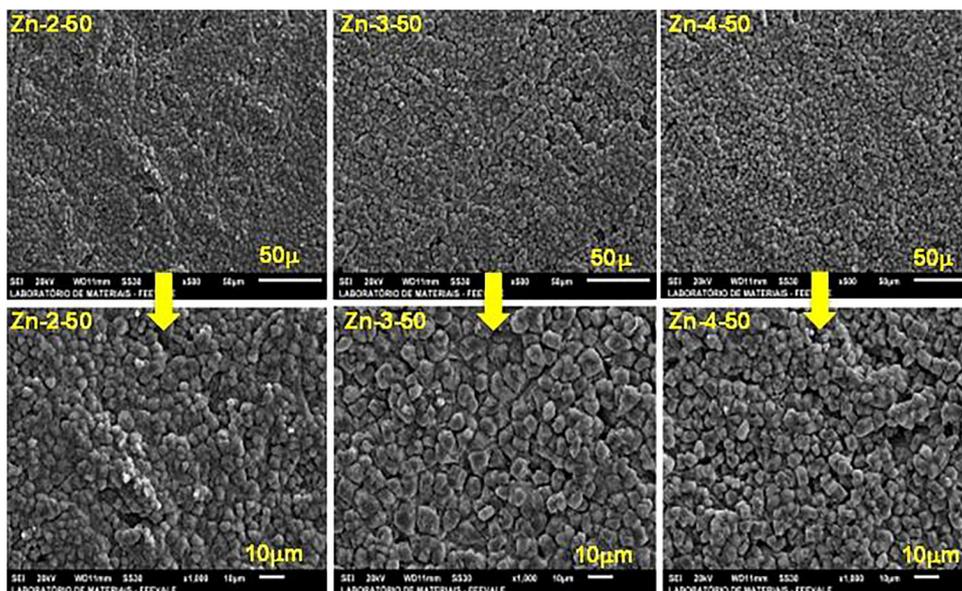


Figure 5: Top micrographs obtained after 2, 3 and 4 minutes of immersion in the phosphating solution at 50°C, using a zinc phosphate conditioner, at magnifications of 500 and 1,000×.

The Ti-2-50 sample, Figure 4, shows regions where the growth of phosphate crystals is not visualized, exemplified by yellow outlines, indicating that the time of 2 minutes was not enough for the complete formation of the layer. However, after 3 minutes of immersion, the Ti-3-50 sample (Figure 4) shows greater coverage of the substrate, indicating that the increase in immersion time favored the nucleation and growth of phosphate crystals. The Ti-4-50 sample, Figure 4, showed coating on its entire surface. This is in line with the layer mass test, where the highest phosphate deposit was measured at 4 minutes (6.38 g/m²) and the smallest deposit at 2 minutes (4.91 g/m²).

Figure 5 shows the top micrographs obtained after 2, 3 and 4 minutes of immersion in the phosphating solution at 50°C, using a zinc phosphate conditioner, at magnifications of 500 and 1,000×.

Samples etched with zinc phosphate show dense coatings at all phosphating times evaluated, with formation of phosphate crystals distributed over the entire surface of the substrate, Figure 5.

It is observed that the phosphating time influences the deposition of phosphate crystals. In this case, a certain amount of time is required for the steps of electrochemical dissolution of the substrate, deposition of the amorphous phase, crystallization and growth of phosphate and the dynamic balance between dissolution and formation of the coating to occur. Insufficient times produce coatings that do not completely cover the substrate and have low deposited mass. Studies conducted by CONGCONG *et al.* [18], in steel samples previously conditioned with titanium solution with phosphating times of 1, 3, 5, 8, 10 and 15 minutes, showed similar results to this work. The phosphating time of 1 minute produced layers with low crystal formation and large regions of porosity. Increasing the immersion time to 3, 5, 8 and 10 minutes caused the crystal size to change, which implied the occurrence of secondary recrystallization, leading to the reappearance of small new crystals. These small crystals quickly grew to form large plate-shaped crystals. After 15 minutes of immersion, the surface was completely covered by phosphate crystals similar to interlocking plates and the phosphate coating became more compact. In the case of this article, despite the deposited mass increasing with immersion time (2min/4.18 g/m², 3min/5.15 g/m² and 4 min/5.38 g/m², respectively), in 2 min. complete coverage of the layer is already obtained.

3.4. Morphological analysis obtained by SEM of the influence of the phosphating temperature

Figure 6 shows the micrographs of the phosphate layers obtained at 40 and 50°C, with immersion time in the phosphating solution of 2, 3 and 4 minutes, using the titanium-based surface conditioner.

It is observed in Figure 6 that the increase in temperature promotes the reduction of phosphate crystals and better surface coverage, influencing the morphology of the phosphate layers. At 40°C, the layers obtained show regions with low density of phosphate crystals, especially at times of 2 and 3 minutes, as exemplified by the outlines in yellow. However, with the increase in temperature to 50°C, a reduction in the size of the formed crystals and a better surface coverage by layer deposition can be visually observed. Ti-3-50 and Ti-4-50 samples present dense layers of phosphate, which reflects in the highest layer mass of 5.91 g/m² and 6.38 g/m², respectively.

Figure 7 shows the micrographs of the phosphate layers obtained at 40 and 50°C, with immersion time in the phosphating solution of 2, 3 and 4 minutes, using the surface conditioner based on zinc phosphate.

It is observed in Figure 7 that there was the formation of dense layers of phosphate, using the zinc phosphate conditioner, both for 40°C and for 50°C. However, at a temperature of 40°C, a greater homogeneity of the crystals is visually observed in the three immersion times evaluated. As for the temperature of 50°C, an increase in the size of the crystals in Zn-3-50 is visually observed, followed by a decrease in the size of the crystals in Zn-4-50. In this case, it is possible that the variation in crystal size, observed in Zn-3-50 and Zn-4-50, is associated with the imbalance between dissolution and coating formation, suggesting that the times of 3 and 4 minutes of phosphatization, at a temperature of 50°C, are excessive.

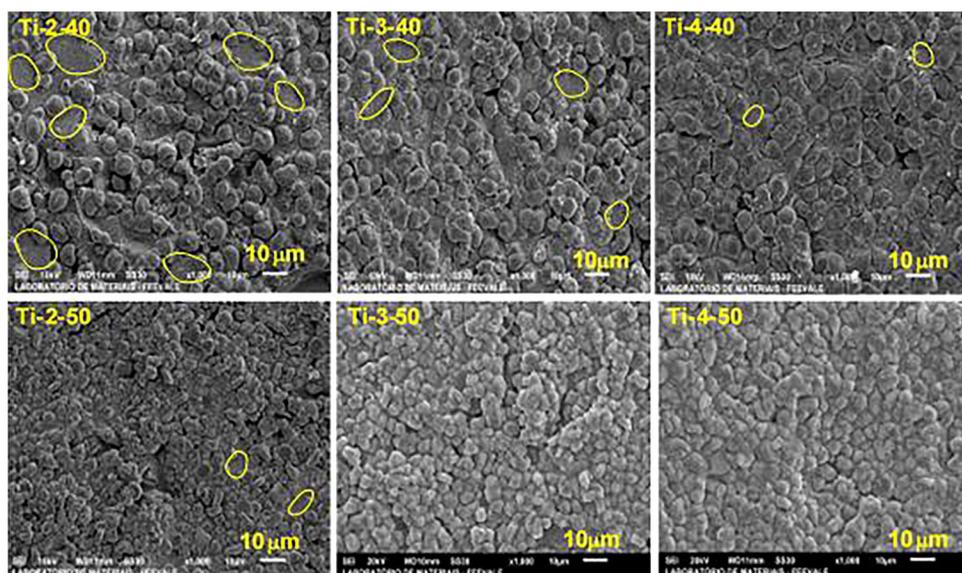


Figure 6: Micrographs in top view obtained using the titanium-based conditioner, with 2, 3 and 4 minutes of immersion in the phosphatizing solution at 40°C and 50°C.

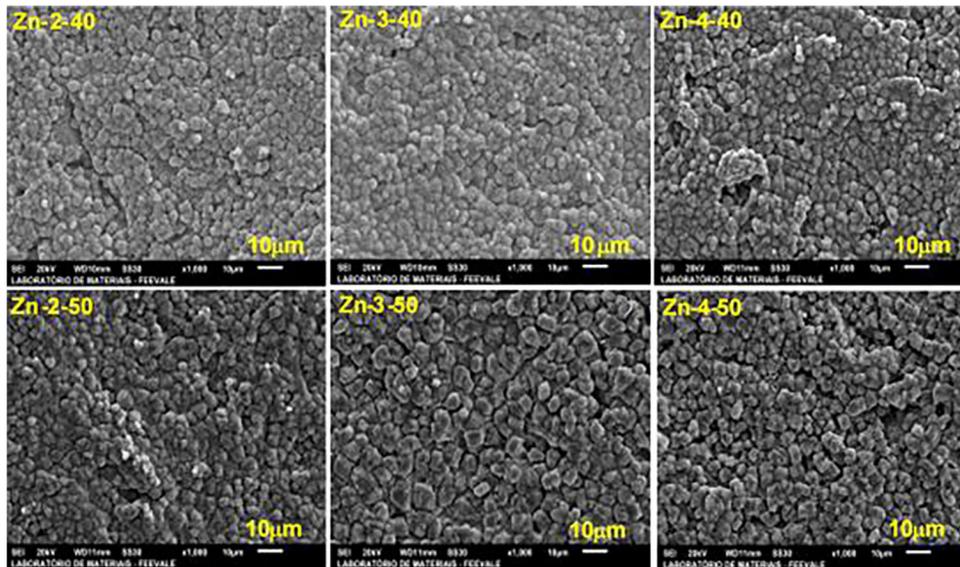


Figure 7: Micrographs in top view obtained using the zinc phosphate conditioner, with 2, 3 and 4 minutes of immersion in the phosphatizing solution at 40°C and 50°C.

Temperature variation was also observed in the deposition of zinc phosphate on steel fibers used in civil construction [20]. Temperatures below 65°C produced coarse coatings, with few phosphate crystal nuclei and which did not completely cover the metallic substrate, due to the slow reaction kinetics. However, samples phosphated at 75°C showed a dense coating, with grain refinement, due to greater nucleation of crystals on the surface at higher temperatures. At a temperature of 85°C, the coating obtained was dense, but with a larger grain size. According to the authors, temperature influences the phosphating process that occurs through continuous layer formation, followed by dissolution and grain growth again.

In the case of this work, with the use of a phosphatization reaction accelerator based on sodium nitrite, the temperatures used were lower than those used by Liu *et al.* [20] and resulted in similar behavior. These results are possibly related to the increase in the equilibrium constant of the phosphatization reaction, which is favored by temperature. The greater the equilibrium constant, the greater the formation of insoluble phosphates that make up the phosphate layer [14].

3.5. Morphological analysis obtained by SEM of the influence of the conditioner in obtaining the layer

Figure 8 compares the micrographs obtained using different titanium and zinc phosphate conditioners, with time if 2, 3 and 4 minutes of immersion in the phosphatizing solution at 40°C.

Comparing the micrographs obtained in Figure 8, one observes the great influence of the conditioner on the formation of the phosphate coating. The coatings obtained using the titanium conditioner showed larger phosphate crystals and partial coverage of the substrate at all immersion times evaluated at a temperature of 40°C. On the other hand, the samples phosphated using the zinc conditioner showed a better refinement of the phosphate crystal, smaller crystals, which favored the formation of dense layers with greater coverage of the substrate.

Figure 9 compares the micrographs obtained using different titanium and zinc phosphate conditioners, with time if 2,3 and 4 minutes of immersion in the phosphatizing solution at 50°C. Figure 9 using the titanium conditioner, show crystal formation on the metallic substrate at all times evaluated. However, the coating obtained with 2 minutes of immersion, Ti-2-50, presented a larger layer-free area than those obtained in 3 and 4 minutes, possibly the surface contact time with the phosphating solution was not enough to complete the phosphating reaction. Samples etched with zinc phosphate showed coatings with greater substrate coverage at all evaluated phosphating times.

The phosphate coatings obtained at 50°C (Figure 9) using the titanium conditioner, show crystal formation on the metallic substrate at all times evaluated. However, the coating obtained with 2 minutes of immersion, Ti-2-50, presented a greater layer-free area than those obtained in 3 and 4 minutes, possibly the contact time of the surface with the phosphating solution was not sufficient to complete the phosphating reaction.

Samples conditioned with zinc phosphate showed coatings with greater substrate coverage at all phosphating times evaluated.

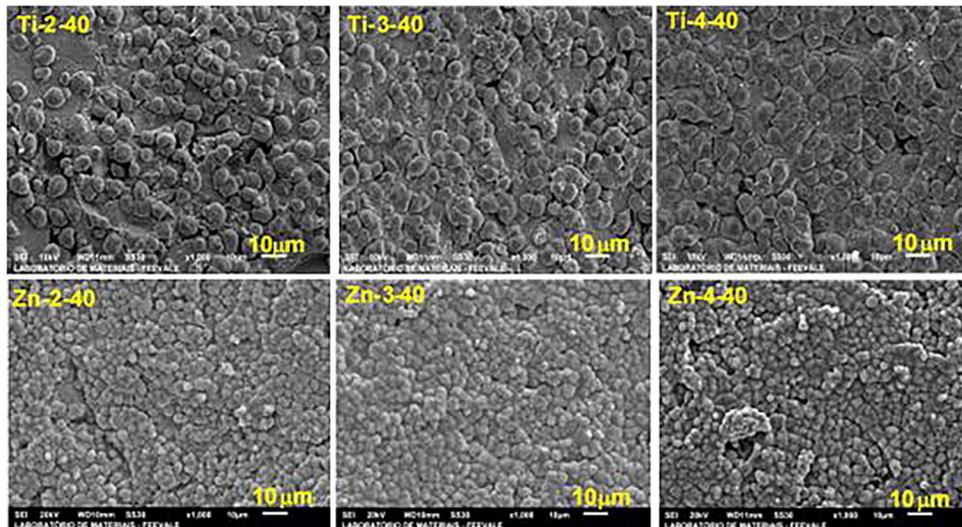


Figure 8: Micrographs in top view obtained using titanium and zinc conditioners, with 2, 3 and 4 minutes of immersion in the phosphating solution at 40°C.

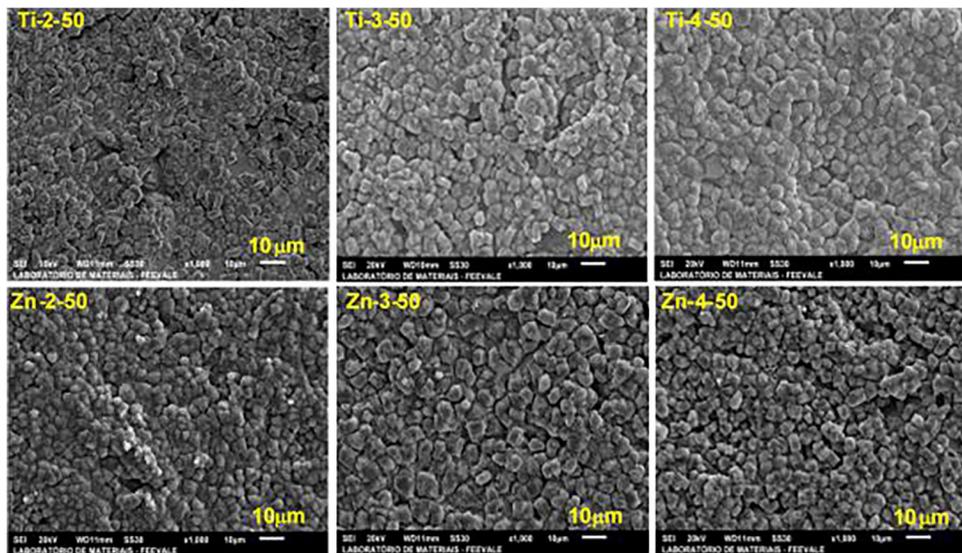


Figure 9: Top view micrographs obtained using titanium and zinc conditioners, with 2, 3 and 4 minutes of immersion in the phosphating solution at 50°C.

Based on the results obtained by SEM, it is observed, in addition to the influence of time and temperature, already mentioned, the contribution of the conditioning agent in the formation of the phosphate layer. In order to demonstrate this contribution in the phosphating process, steel samples were phosphated without the use of conditioning agents, as shown in Figure 10. For comparison purposes and better analysis, the SEM micrographs of the Ti-3-40 and Zn-3-40 (Figure 8) and Ti-3-50 and Zn-3-50 (Figure 9) were again shown in the sequence of Figure 10.

Figure 9 shows the appearance of the surface of the substrate without phosphating and after 3 minutes of phosphating at 40 and 50°C, without the use of a conditioning agent. The phosphatization did not occur homogeneously, with low formation of crystals on the surface of the samples, with a large part of the exposed substrate remaining, making evident the influence exerted by the conditioning agent on the formation and refinement of the phosphate crystals when compared with the micrographs in the Figure 10, which shows a dense layer of coating.

The influence of different surface conditioners was investigated by Li *et al.*, [14] when comparing titanium, oxalic acid and phosphoric acid conditioners in the phosphating process of magnesium alloys with

manganese phosphate. The authors observed that the phosphating time is influenced by the previous conditioning of the surface, which agrees with the results of this work. The phosphating obtained from acidic, oxalic and phosphoric conditioners generated a smaller crystal size and greater surface coverage compared to that obtained using the titanium conditioner. The author attributes the best performance of acidic solutions in surface conditioning to the removal of the oxide film, anticipating the first stage of phosphatization, consequently reducing the time required for the complete coating deposition reaction. In the case of this work, as zinc phosphate is present in the conditioning agent, it is believed that the incorporation of zinc from the phosphatizing solution may have favored better deposition.

3.6. Determination of deposited mass of phosphate for a time of 1800s

Based on the SEM results obtained from samples phosphated at 50°C, and with the aim of verifying the behavior of phosphate deposition over time, extrapolating the range recommended by the manufacturer of 120 to 240s of substrate contact with the phosphating solution, new samples were phosphatized using titanium or zinc conditioner, at different times up to 1800s, and the masses of the coating obtained are shown in Figure 11.

It is observed that the phosphate layer deposited more quickly in the initial seconds of immersion with the use of the zinc conditioner. When evaluating the micrographs obtained by SEM, Figure 10, of the coatings formed with the use of the two conditioners, a better coverage of the substrate is observed with the use of the zinc phosphate conditioner in the shortest time (2 minutes), agreeing with the results obtained in the gravimetric curve (Figure 11) which shows a greater deposition in the initial seconds of phosphating with the use of this conditioner. The zinc phosphate conditioner provides greater nucleation of the phosphate crystals, covering the substrate more quickly and consequently forming crystals of reduced size and layers with lower mass. On the other hand, surfaces etched with titanium salts require a longer phosphating time for complete coverage of the substrate and present a greater deposit of the phosphate coating.

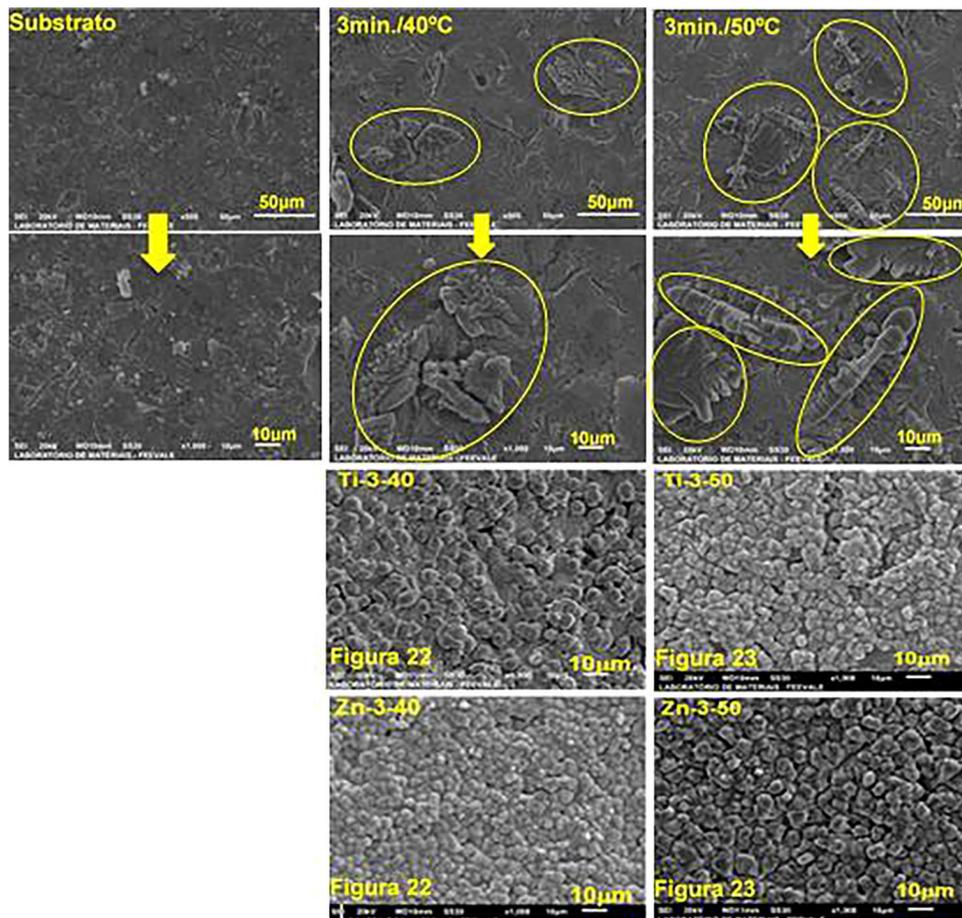


Figure 10: Micrographs in top view of the sandblasted metallic substrate, samples phosphated at 3 minutes/40°C and at 3 min./50°C, without the use of surface conditioner, at different magnifications.

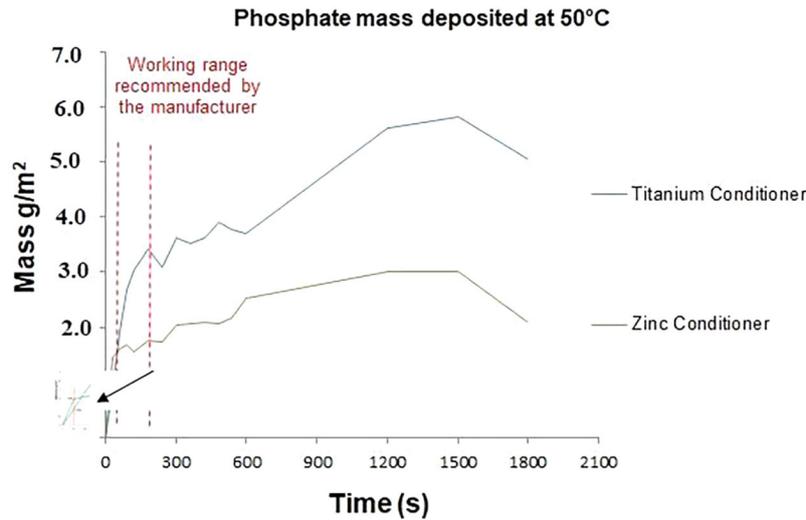


Figure 11: Gravimetric curve of deposited phosphate masses for titanium and zinc conditioners at 50°C.

In 120 s, the minimum phosphating time recommended by the manufacturer, the phosphate layer obtained with the use of the titanium-based conditioner is 3.0251 g/cm², while with the use of the zinc phosphate conditioner it is 1.5629 g/cm², showing little variation in relation to the initial 30 s. In this case, a slower deposition is observed with the use of the titanium conditioner, as it requires a longer time to completely cover the substrate.

In 240 s, the time limit stipulated by the manufacturer for phosphating, there is little increase in the deposited mass, both for titanium and zinc, remaining practically linear until approximately 1550 s.

In addition, in the initial 30 s of immersion, according to the magnification, it is observed that the mass of phosphate deposited using the titanium conditioner is 0.8949 g/m² and with the use of zinc phosphate conditioner is 1.4607 g/m². For the mass of phosphate obtained using the titanium conditioner to equal that of zinc (1.4607 g/m²) it would take 50 s of process instead of 30 s. However, after 30 s, a stabilization of the phosphate layer is observed, with little variation in the deposited mass, with the use of the zinc phosphate conditioner, unlike the layer obtained with the use of the titanium conditioner, which continues to increase linearly, having its value doubled in 60 s in relation to the first 30 s.

3.7. Electrochemical analysis using open circuit potential

The OCP curve of phosphate layer formation was obtained by immersing samples in tricationic zinc phosphate phosphating solution at a temperature of 50°C. For this purpose, three types of samples were immersed in the phosphatizing solution: one of pure SAE 1010 carbon steel, one of SAE 1010 carbon steel etched with titanium etching agent and one of SAE 1010 carbon steel etched with zinc phosphate etching agent. The graph obtained from the OCP curves is shown in Figure 12.

Figure 12 shows the stages of formation of the phosphate coating. Initially, an abrupt shift of the potential from approximately 0.15V to a value around -0.60V is observed, for previously conditioned samples, and -0.55V for the pure steel substrate. This first stage corresponds to the electrochemical attack on steel in all evaluated samples. The pure SAE 1010 steel sample, without surface conditioning, does not show potential variation that indicates the formation of the coating, however, as shown in Figure 12, it occurs, but slowly, which can be seen in the expansion of the graph. Samples etched with titanium or zinc, due to the influence of previous surface conditioning, show an increase in potential with immersion time, making the phosphating reaction faster, in agreement with the top micrographs obtained by SEM, shown in Figure 9.

The sample previously conditioned with zinc phosphate presents a potential variation of -0.60V to -0.50V, after an immersion time of approximately 280s, in which the formation of the phosphate layer occurs. However, the formation of the coating obtained with the use of the titanium-based conditioner also varies from -0.60V to -0.50V, but with a longer time, around 310s. This result agrees with those obtained in the gravimetric curve, Figure 11, in which the greater deposition of the layer in the initial seconds in the sample etched with zinc phosphate was evidenced. The coatings obtained with the use of the two conditioners present dynamic balance between formation and dissolution at -0.50V, from 280s for conditioning with zinc phosphate and, from 310s for conditioning with titanium salts.

3.8. Electrochemical analysis using potentiodynamic polarization

Figure 13 shows the graph of the electrochemical tests of potentiodynamic polarization carried out in 0.01M NaCl electrolyte obtained from the pure carbon steel substrate and from the phosphated samples. The samples were previously conditioned with a titanium-based or zinc phosphate-based solution, and phosphatized at temperatures of 40 or 50°C, for 2, 3 and 4 minutes.

According to the curves in Figure 13, it is observed that all phosphating conditions with conditioning agents shifted the potential to more positive values and lower corrosion current densities compared to untreated steel, indicating that the coatings improve corrosion resistance. However, the coatings present different behaviors among themselves.

In Figure 12, it is observed that the increase in the phosphating time shifts the corrosion potential to more noble potentials with the use of the titanium conditioner. However, this displacement is approximately 50 mV, which can be inferred that there is almost no difference between the potentials. However, it was found that the corrosion current density decreases approximately one order of magnitude with increasing phosphating time to 3 min. and then increases again in 4 min. However, Ti-3-40 was not expected to present a lower corrosion current density than the other samples, since there was a low coverage of the substrate by the coating, according to the micrographs obtained by SEM, Figure 2. The phosphating times used, 2, 3 and 4 minutes, at 40°C, were not enough for the formation, refinement and growth of phosphate crystals on the metallic surface in order to cover it completely, thus allowing a greater exposure of the substrate to the corrosive agent.

It is also observed in the polarization curves (Figure 13) that the increase in the phosphating temperature to 50°C favored the displacement of the corrosion potential to nobler potentials compared to the curves obtained at 40°C and reduced the corrosion current density. According to the graph, this shift was approximately 150 mV for the Ti-3-50 sample compared to the uncoated steel. This is related to the greater coverage of the substrate and the formation of small-sized crystals observed in the micrographs obtained by SEM in Figure 4. Samples phosphatized at 50°C have a greater mass deposited in relation to the phosphatization temperature of 40°C, which gives the substrate greater resistance to corrosion. The Ti-3-50 sample has a better performance against corrosive solution attack when compared to the Ti-4-50 sample, suggesting that the time of 4 minutes is longer than necessary for the formation of the phosphate coating, and consequently its corrosion protection is reduced. The time of 2 minutes (Ti-2-50), as observed in the micrographs obtained by SEM, Figure 4, presents regions free of layer that reflect in its lower resistance to corrosion.

By analyzing the graph of the polarization curves (Figure 13) obtained for the pure carbon steel substrate sample and the phosphated samples at times of 2, 3 and 4 minutes, at 40°C, using the zinc conditioner, it is observed that the coating obtained with the use of the zinc phosphate conditioner shifted the sample potentials to nobler values (approximately 210 mV) and decreased the corrosion current density compared to the uncoated steel. However, the sample with the shortest time, 2 minutes, gave the substrate better resistance to corrosion compared to the times of 3 and 4 minutes, which was not expected, because according to the SEM images, Figure 4, and the deposited mass analysis the phosphating time favors obtaining denser layers with greater mass. The literature indicates that already in the initial seconds of phosphating there is a rapid formation of FePO_4 and Fe_2O_3 that acts as an amorphous layer on the surface of the steel [18]. This was observed in the gravimetric curve

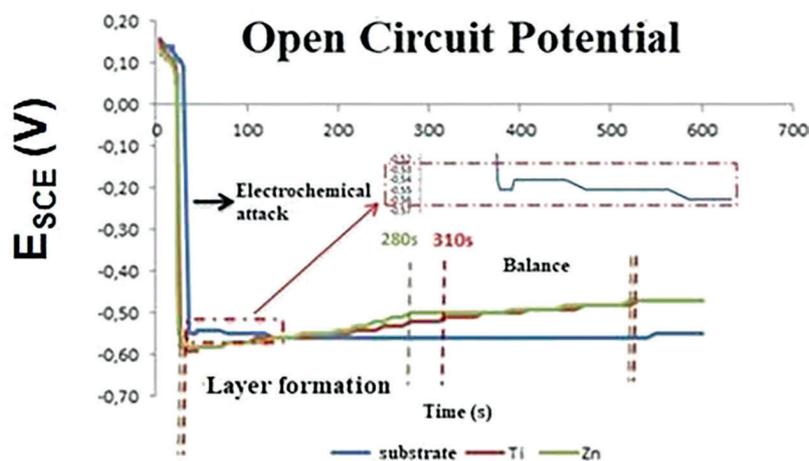


Figure 12: Open circuit potential of the SAE 1010 steel substrate without and with the use of titanium-based conditioner or zinc phosphate-based conditioner, phosphated at 50°C.

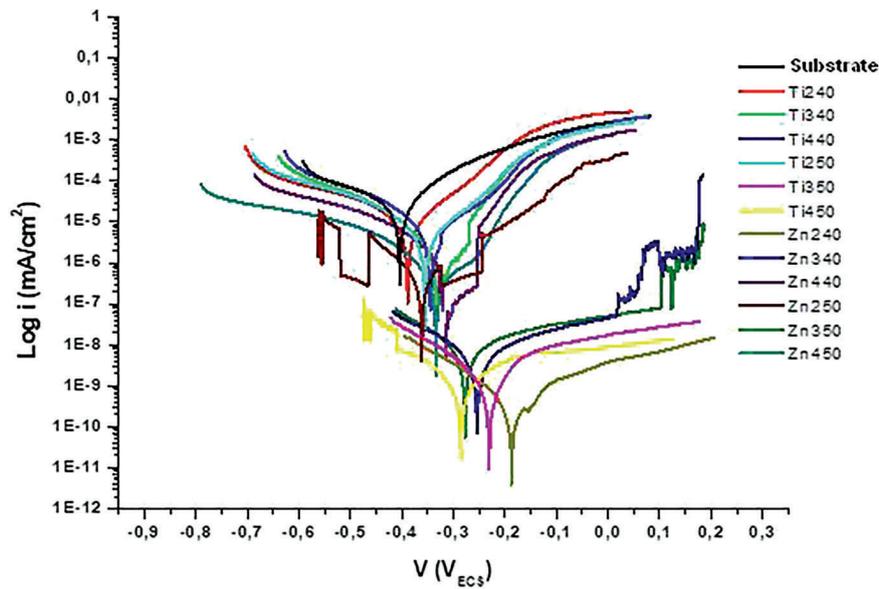


Figure 13: Polarization curves of phosphatized samples at times of 2, 3 and 4 minutes, at 40 and 50°C, with the use of conditioners based on titanium or zinc phosphate.

of Figure 13, in which the coating layer practically reached its maximum value in the first 30 s of immersion in the phosphating solution with the use of the zinc phosphate conditioner. As reported by ASADI *et al.* [21] a certain immersion time is required for the layer to be deposited on the steel surface and produce an adequate thickness for protection against corrosion, with the complete coating of the substrate. However, if the immersion time is too long, the quality and protective properties of the coating decrease due to the growth of phosphate in the coating, leading to internal stresses that decrease its toughness, increasing porosity and cracking. Therefore, the longer phosphating time may have favored the mass increase, but not the density, leaving the coating with irregularities on the surface, which would explain the lower anticorrosive performance with increasing immersion time in the phosphating solution.

On the other hand, if we analyze the polarization curves of the pure carbon steel substrate sample and the samples phosphated in the times of 2, 3 and 4 minutes, at 50°C, with the use of the zinc conditioner, they indicate that the increase in the immersion was not the determining factor for obtaining layers more resistant to the corrosive environment, since the Zn-4-50 coating does not present the greatest displacement of the corrosion potential or the lowest current density compared to the uncoated sample. The coatings obtained with 2 and 4 minutes of immersion (Zn-2-50 and Zn-4-50) have similar corrosion potential and corrosion current density. However, the Zn-3-50 sample presents a greater displacement of the corrosion potential, approximately 120 mV in relation to pure steel and the lowest corrosion current density. As with the phosphated samples at 40°C, it was expected that the samples obtained at 50°C would show better anticorrosive behavior with increasing immersion time, since the coating mass increases with increasing time.

4. CONCLUSIONS

From the results obtained, it was found that increasing the phosphating temperature from 40°C to 50°C, using the titanium conditioner, is more suitable for providing greater layer deposition and producing smaller crystals. However, when using the zinc phosphate-based conditioner, the temperature of 50°C led to the formation of larger phosphate crystals than at the temperature of 40°C, the latter being the best phosphating condition. Reducing the phosphotization temperature with the use of zinc phosphate-based conditioner is the major difference in the industrial environment for replacing the titanium-based conditioner, currently highly widespread in phosphotization processes. In the literature, zinc phosphate is reported as an option for use as a conditioning agent, however, no articles were found describing its use.

In comparison with the corrosion resistance of the phosphated layers obtained with the use of the 2 conditioners, the best phosphating condition was obtained with the zinc conditioner at 40°C and the titanium conditioner at 50°C, therefore requiring a 10°C increase in phosphating temperature to provide similar corrosion resistance between both layers.

5. ACKNOWLEDGMENTS

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