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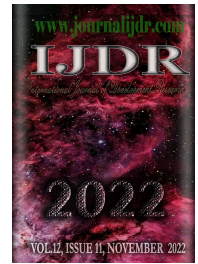
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RESEARCH ARTICLE

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CONVERSION LAYERS SUBSTITUTED TO HEXAVALENT CHROME IN THE ANTI-CORROSION PROTECTION OF GALVANIZED STEEL

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ABSTRACT

Metals/metal alloys are among the most used materials in the industrial environment. Among these, ferrous alloys have been widely applied in different segments of the industry such as: automotive, chemical, oil and gas, etc. Due to the different environmental conditions in which this material is applied, there are situations that can cause steel degradation, in a phenomenon known as corrosion. The degradation of the metal by the effect of corrosion generates environmental and economic impacts, which cause a decrease in the cost-benefit ratio. In order to reduce these losses, several protection methods are used such as corrosion inhibitors, passivates and paints. The galvanization of steel is widely used in the metallurgical industry as a metallic coating for protection, where it presents a considerable increase in the useful life of the material and because it is economically viable. In turn, chromating is a procedure performed on metallic coatings in order to prolong the useful life of these materials. However, this method uses chromate ions as a source of passivation, which are known to have high toxicity and carcinogenic effects. The search for new passivators that replace hexavalent chromium and present less toxicity is necessary. In this work, galvanized steel samples were passivated with two possible substitutes for hexavalent chromium: Molybdate and Permanganate. The corrosion resistance of the conversion layers was verified by electrochemical tests of polarization curve, open circuit potential, chronoamperometry and impedance. For comparison purposes, the tests were also performed in dichromate solution. Through the comparative evaluation of the corrosion resistance of galvanized steels with or without conversion coatings, it was verified that both the permanganate and the molybdate coatings presented a good potential for replacing Hexavalent Chromium. However, under the experimental conditions tested, the conversion to permanganate showed more significant results than to molybdate.

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INTRODUCTION

The corrosive process consists of the deterioration of materials by the chemical or electrochemical action of the environment, causing considerable damage to the metallic structure, causing, in addition to economic losses, accidents and contamination to the environment. There are several ways to minimize the effects caused by corrosion and among the main methods used we can mention the organic and metallic coatings (GENTIL, 2007). Despite remarkable advances in the field of corrosion science and technology, the phenomenon of corrosion remains a major obstacle for industries across the world. Thus, industries are in need of cheap metallic materials along with an

adequate protection method. Thus, it is necessary to apply methods and strategies that can inhibit or minimize corrosion, and metallic coatings have interesting characteristics that make them attractive for application as protective coatings, alone or combined with other types of coating. Among the class of metallic coatings, the galvanizing procedure of steel is widely used in the metallurgical industry to increase corrosion resistance, as it presents a considerable increase in the useful life of the material and is economically viable. Galvanization consists of coating steel with a thin layer of zinc (TANG *et al.*, 2012; GENTIL, 2007). Zinc and zinc-based alloys have been widely applied for corrosion protection of metallic substrates. However, zinc-based alloys pose a challenge for corrosion protection, as they do not form a spontaneously passivating oxide film to retard corrosion in an aggressive environment, unlike other active light

metals such as Al and Ti. al., 2017 – XU *et al.*, 2018). Corrosion of galvanized steel can be inhibited by different methods, including corrosion inhibitors, paints, anti-corrosive oils and passivates. Passivation, also known as the conversion layer, protects the material from corrosion and favors the adhesion of organic coatings. Among zinc passivates, hexavalent chromium (Cr-VI), in the form of chromate ion, has been the most used and efficient for decades. Chromatization is an example of a post-treatment strategy used to increase the shelf life of zinc coatings (DI SARLI *et al.*, 2014). This procedure consists of a process that promotes an increase in the corrosion resistance of galvanized steel by immersing the material in chromic acid or solutions containing chromate ions. In addition, hexavalent chromium has barrier properties and self-regenerative capacity (JIAN *et al.*, 2015). However, despite the many benefits of Cr-VI, its use has been reduced since this element has carcinogenic and mutagenic effects in animals. Substitution for components with less toxicity is the focus of several researchers who seek an inhibition efficiency similar to chromium, and these substitutes must combine increased corrosion resistance, low toxicity and a good cost-benefit ratio. Among the most studied compounds are trivalent chromium, permanganates, vanadates, molybdates, dichromate, among others.

Several studies have reported conversion coating technologies as an alternative and these are extensively investigated, through analyzes of physical and mechanical properties, porosity, adhesion to the base metal or top coating, and heat or low temperature resistance as well as corrosion resistance. and protective properties of zinc substrates (GAO *et al.*, 2018). Research has been carried out, in which different types of substances are tested as passivation, not only of galvanized steel, but also of aluminum and magnesium alloys, and some baths containing, for example, the presence of vanadate ions, tungstate, earth metal ions rare, molybdates, phosphates, silanes, and some organic anions have a low toxicity character combined with inhibitory properties, being therefore considered as potential alternatives for the replacement of chromate ions (DI SARLI *et al.*, 2014; LI *et al.*, 2013; ZOU *et al.*, 2011; GOURU *et al.*, 2015 & TSAI *et al.*, 2010). Considering the wide application of galvanized steel and the importance of using conversion layers in order to increase the corrosion resistance and adhesion profile of these coatings, this work evaluated the application of molybdate and permanganate ions as substitutes for hexavalent chromium in baths. conversion on galvanized steel. In this context, the objective of the article was to obtain conversion layers on galvanized steel from passivation baths free of chromate ions, aiming at increasing the corrosion resistance of these metal alloys and reducing the environmental impact caused by the high toxicity of chromium ions (VI).

MATERIALS AND METHODS

Preparation of specimens: The metallic alloys used in this project consisted of commercial samples of galvanized steel, commonly used in the industrial environment. The samples were machined in the form of plates in the dimensions 3 x 3 cm. After machining, the steel samples were subjected to a pre-treatment before passivation. This treatment consists of degreasing the samples in an alkaline solvent, washing in distilled water and drying with cold air and storing in a desiccator. The machining and pre-treatment steps of the samples were carried out in the LDM and LTM laboratories, both located in UERJ.

Preparation of passivation baths: The passivation baths were prepared using analytical grade reagents containing permanganate, molybdate and dichromate ions. The acidification of the bath was obtained by adding phosphoric acid, and the bath temperature was maintained at 25°C. To obtain the conversion layers, the galvanized steel samples were activated in 1% HNO₃ for 7 seconds. Then the samples were immersed in the conversion baths with the conversion time in 300 s. After immersion, the samples were dried in an oven at a temperature of 80°C for 30 minutes. The step of obtaining the conversion layers was carried out in the LTM laboratory located at UERJ. 3 passivation baths were prepared, all with a concentration of

15 g/L, 30 g/L and 100 g/L and pH 1.5 (adjusted with 50% phosphoric acid) from the following analytical reagents.

Electrochemical Tests: The corrosion resistance of the samples was evaluated by obtaining electrochemical tests that consisted of open circuit potential measurement, potentiodynamic and potentiostatic polarization curves and electrochemical impedance spectroscopy. The electrochemical tests were carried out in an aerated 3.5% NaCl solution at room temperature. A cell with three electrodes was used: reference electrode – calomel, counter electrode – platinum spiral, working electrode – galvanized steel with and without conversion treatment. All electrochemical tests were performed using an AUTOLAB potentiostat/galvanostat, model PGSTAT302N. These tests were carried out at the LPPM laboratory located in UERJ. Initially, the open circuit potential of the samples was monitored for 1 hour after immersion in 3.5% NaCl solution. The polarization curves were obtained after evaluating the open circuit potential in each of the tested experimental conditions. Potentiodynamic polarization was performed after stabilization of the open circuit potential, at a sweep speed of 1 mV/s in a potential range of +/- 1.5 V in relation to the open circuit potential. Potentiostatic polarization (current x time) was performed at specific potentials, chosen by evaluating the potentiodynamic curve for a time of 3600s. The potentials were chosen after evaluating the potentiodynamic polarization curve. Electrochemical impedance tests were performed at open circuit potential, for a concentration of 30 g/L, using an amplitude of 10 mV (rms) and in a frequency range ranging from 10 KHz – 7 mHz.

Scanning Electron Microscopy: The surface morphology of the samples with and without the conversion treatments were obtained through a scanning electron microscope brand JEOL JSM 6490LV, using radiation in the secondary electron mode. The micrographs were performed in the scanning electron microscopy laboratory at UERJ.

RESULTS AND DISCUSSION

Figures 1 to 3 present the results of the evolution of the open circuit potential of the galvanized steel samples in 3.5% NaCl solution, with and without the presence of the conversion layers obtained in the different concentrations of the baths containing the dichromate, permanganate ions and molybdate.

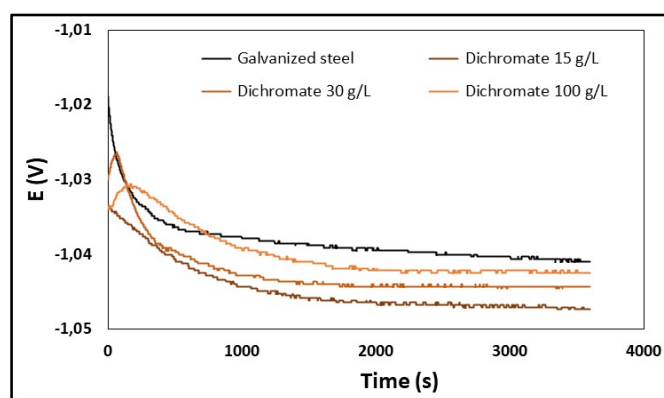


Figure 1. Evolution of the open circuit potential of galvanized steel with and without the presence of conversion layers obtained in solutions containing dichromate ions

It is possible to verify that the conversion treatment caused a shift from the open circuit potential to more cathodic (more negative) potentials, this shift is less significant for molybdate conversion coatings compared to dichromate and permanganate. Table 1 presents the open circuit potential values for the samples with and without the conversion treatment. It is verified that the permanganate conversion treatment caused the greatest displacement of the open circuit potential.

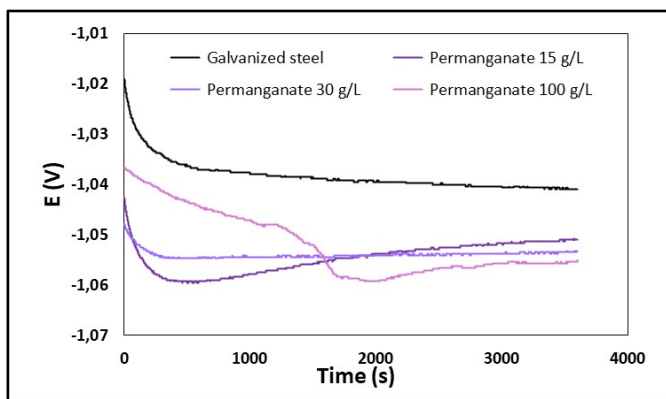


Figure 2. Evolution of the open circuit potential of galvanized steel with and without the presence of conversion layers obtained in solutions containing permanganate ions

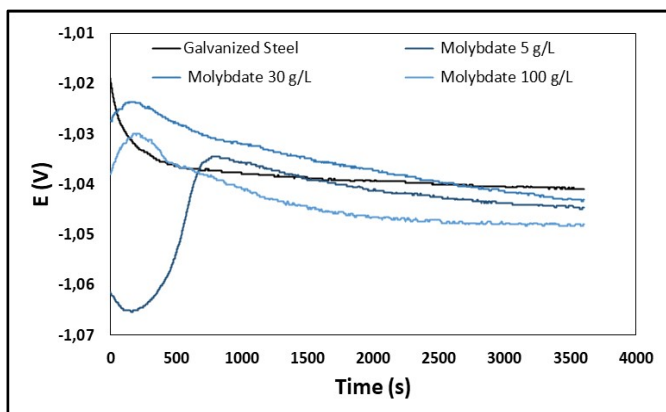


Figure 3. Evolution of the open circuit potential of galvanized steel with and without the presence of conversion layers obtained in solutions containing molybdate ions

Table 1. Open Circuit Potential for steel with and without conversion treatment in NACL medium 3.5%

ConversionLayer	Open Circuit Potential
Galvanizedsteel	-1,019V
Galvanized steel + Dichromate 30g/L	-1,03V
Galvanized steel + Dichromate 100 g/L	-1,033V
Galvanized steel + Permanganate 30 g/L	-1,048V
Galvanized steel + Permanganate 100g/L	-1,036V
Galvanized steel + Molybdate 30 g/L	-1,027V
Galvanized steel + Molebdate 100 g/L	-1,037V

The coatings obtained in a bath containing molybdate ions showed a significant reduction in current only at the highest concentration used (100 g/L), as can be seen in Figures 4 to 6. A reduction in current is observed in the three potentials evaluated, however at the potential corresponding to the passivation region ($E = 0.2$ V), the current reduction was more significant. This behavior is an indication that the conversion layer obtained in molybdate media promotes the formation of a passive film on the surface of the sample, causing the reduction of the current, and consequently increasing the corrosion resistance. The reduction in current is more significant in the first 500 s, after this period of time the current rises again, reaching a plateau. The conversion treatment in the presence of permanganate ions observed in Figures 7 to 9, showed better results at the intermediate concentration (30 g/L), that is, under the evaluated experimental conditions there is an optimal concentration in which the anticorrosive properties of the layer are maximized. The greatest current reduction is observed at the most applied anodic potential (0.2 V), this behavior is similar to that observed for molybdate coatings. The results obtained for comparative purposes in the presence of dichromate, shown in Figures 10 to 12, show that, in the same way as

permanganate, the most significant results are verified for the concentration of 30 g/L.

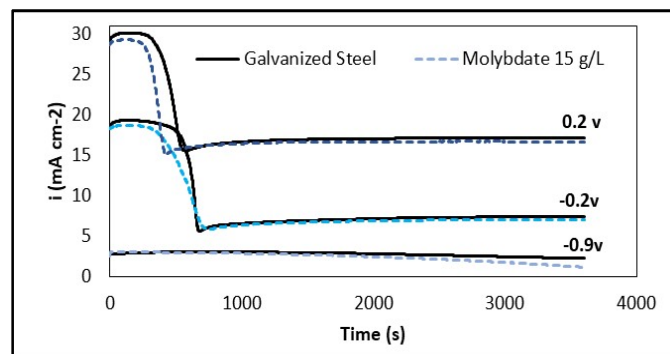


Figure 4. Potentiostatic polarization curves obtained for galvanized steel with conversion treatment in molybdate baths (15 g/L)

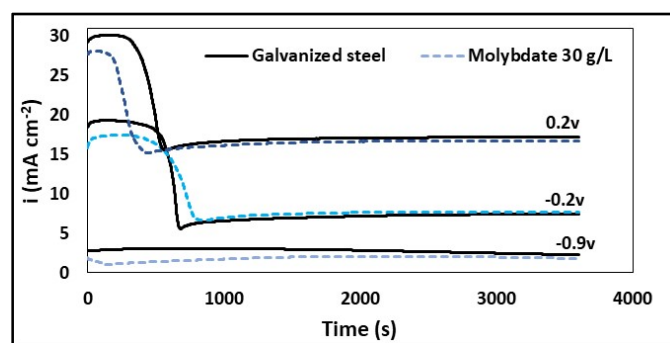


Figure 5. Potentiostatic polarization curves obtained for galvanized steel with conversion treatment in molybdate baths (30 g/L)

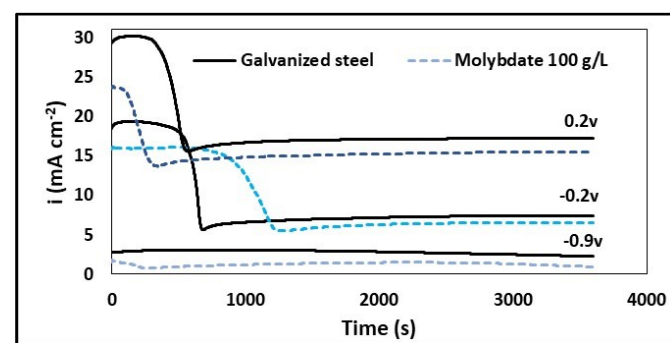


Figure 6. Potentiostatic polarization curves obtained for galvanized steel with conversion treatment in molybdate baths (100 g/L)

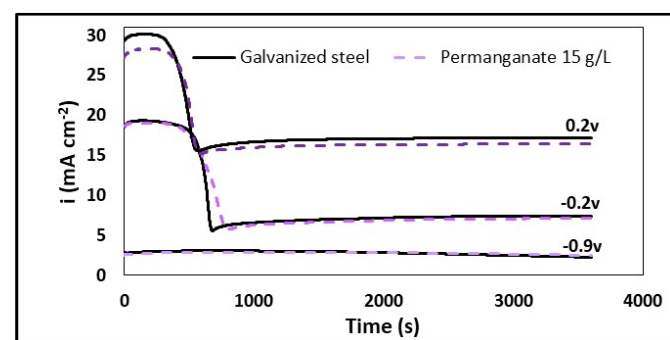


Figure 7. Potentiostatic polarization curves obtained for galvanized steel with conversion treatment in permanganate baths (15 g/L)

However, in the other concentrations, a reduction in the current was also observed, especially for the potential of 0.2 V.

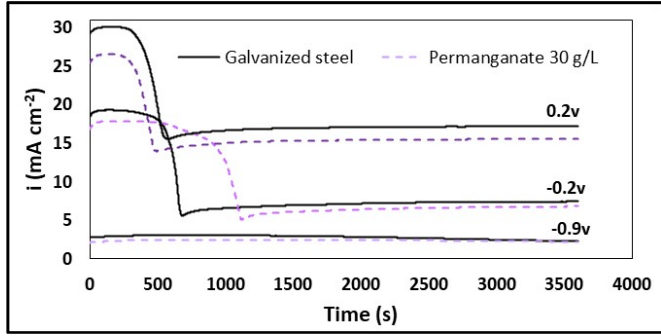


Figure 8. Potentiostatic polarization curves obtained for galvanized steel with conversion treatment in permanganate baths (30 g/L)

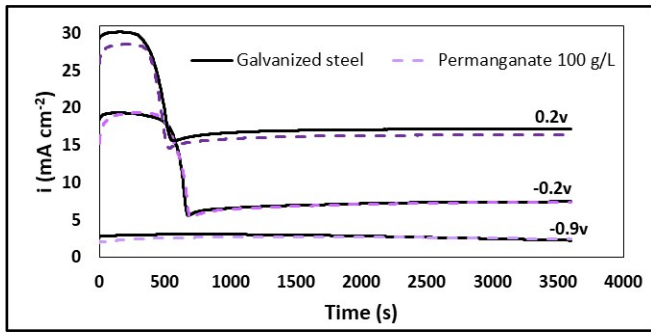


Figure 9. Potentiostatic polarization curves obtained for galvanized steel with conversion treatment in permanganate baths (100 g/L)

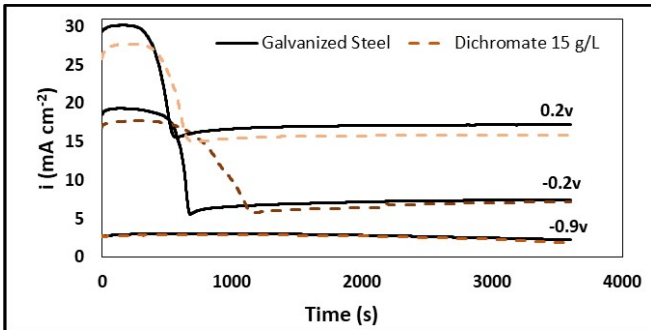


Figure 10. Potentiostatic polarization curves obtained for galvanized steel with conversion treatment in dichromate baths (15g/L)

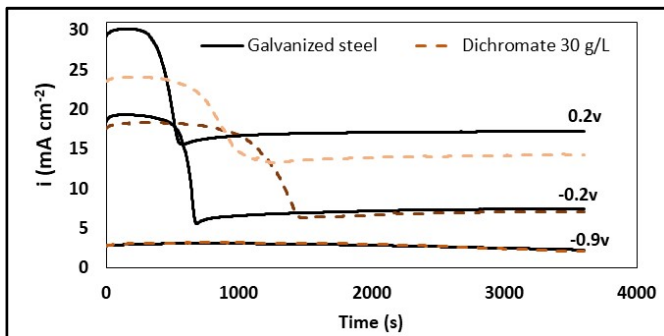


Figure 11. Potentiostatic polarization curves obtained for galvanized steel with conversion treatment in dichromate baths (30 g/L)

These results are an indication that both molybdate and permanganate constitute promising alternatives for the replacement of hexavalent chromium ions in obtaining layers conversion on galvanized steel.

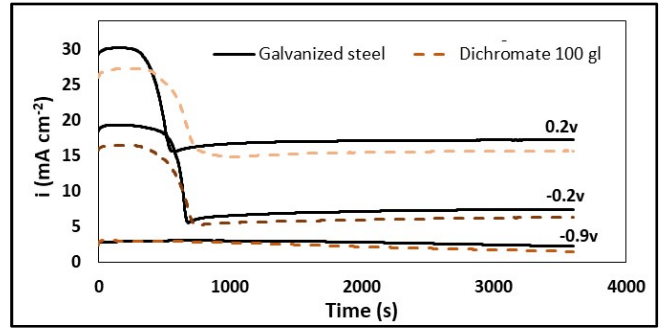


Figure 12. Potentiostatic polarization curves obtained for galvanized steel with conversion treatment in dichromate baths (100 g/L)

However, the performance of the layers is extremely dependent on the conversion bath conditions, and the experimental results obtained show that each type of anion has a set of factors that will influence the formation of the passive film and consequently the corrosion resistance. The electrochemical results are supported by the scanning electron microscopy obtained for the galvanized steel samples with and without the conversion treatments.

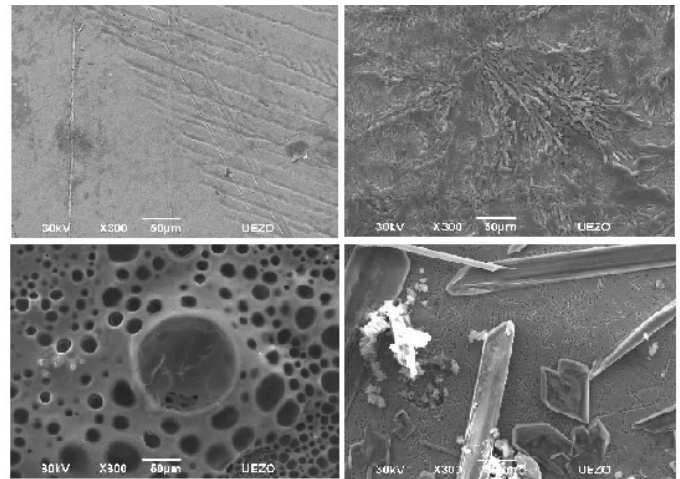


Figure 13. Observation of the surface morphology of galvanized steel with and without the presence of conversion layers at a concentration of 30 g/L: a) galvanized steel, b) treated with dichromate, c) treated with molybdate and d) treated with permanganate

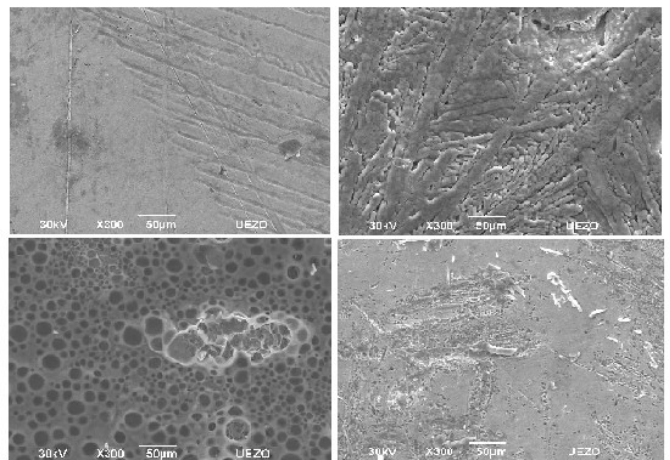


Figure 14. Observation of the surface morphology of galvanized steel with and without the presence of conversion layers at a concentration of 100 g/L: a) galvanized steel, b) treated with dichromate, c) treated with molybdate and d) treated with permanganate

The morphology of the layers obtained was observed by scanning electron microscopy under the experimental conditions (30g/L and 100g/L) previously presented and can be seen in Figures 13 and 14. It is possible to clearly verify that in both concentrations evaluated, if the formation of a layer on the steel surface and that the morphology of the layer differs in relation to the anion used in the passivation bath. The layers formed in the presence of dichromate present the formation of a morphology with a dendritic appearance, and in both concentrations the layer appears to be relatively integrated and compact. The conversion treatment in the presence of molybdate resulted in the formation of layers with morphology where pore formation is observed at concentrations of 30 and 100 g/L. However, despite the porosity, it is possible to verify that the surface of the galvanized steel is covered, and this film is responsible for the increase in corrosion resistance. The morphology of the layers obtained in permanganate also differs from the others, in this case a less homogeneous morphology is observed with the presence of deposits in the form of needles and plates on the surface of the sample. However, despite the lower homogeneity, it is possible to verify that the surface is covered and there are no apparent pores as in the samples treated with molybdate. The micrograph corroborates the electrochemical results in which it was verified that the samples treated in permanganate medium presented corrosion resistance compatible with the samples converted in conventional dichromate baths. The differences in the morphology of the formed layers are probably directly related to the electrochemical behavior of the samples under the evaluated experimental conditions and, consequently, to the corrosion resistance. It is possible to state that in all cases there was the formation of a layer on the surface and that this promoted an increase in corrosion resistance. The layers obtained in the presence of dichromate and permanganate appeared to be more compact and homogeneous when compared to those obtained in the presence of molybdate, this difference may be responsible for the greater corrosion resistance of these coatings. However, even with the presence of porosities, the conversion treatment in the presence of molybdate promotes an increase in corrosion resistance when compared to the untreated samples. Thus, it is possible to affirm that both permanganate and molybdate can be interesting alternatives to the substitution of hexavalent chromium ions in the conversion baths. However, a more in-depth evaluation of the experimental conditions for obtaining the conversion layers and their relationship with the increase in corrosion resistance is necessary.

CONCLUSION

The results obtained showed that the conversion baths consisting of molybdate and permanganate ions can promote the formation of conversion layers on the surface of galvanized steel, increasing the strength of this steel in relation to the sample without conversion layer. The effect of the conversion bath composition (anion concentration effect) on the conversion layers showed that there is an ideal concentration for each type of anion. For the baths based on dichromate and permanganate the concentration of 30 g/L presented more significant results, for the molybdate the best results were observed at the concentration of 100 g/L. The analysis of the morphology of the layers showed that the conversion coatings obtained from baths containing dichromate and permanganate are more compact and homogeneous than those obtained from molybdate.

Under the experimental conditions evaluated, it is possible to state that both baths containing permanganate and baths containing molybdate can be promising alternatives to the use of hexavalent chromium ions. However, a systematic study of the conditions and factors that influence the bath and the quality of the conversion layers is necessary.

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