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PERFORMANCE COMPARISON OF PRE-COATING FOR REPLACEMENT OF PHOSPHATING[1]

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Abstract

The corrosion protection of steel structures through the application of organic coatings is obtained using a complex pre-treatment prior to paint. Pre-treatment of metal, as primer, intermediate and top coat, are the layers that make up the protection system. Although pre-treatment of chromate and phosphate are used widely, the procedures require alternative solutions to the toxicity of chromium sludge and the effluent phosphate. This fact led to the development of new pre-treatment. In this study, the new pre-treatments based on Zr and Ti/Zr complex were applied to steel substrates and coated with an organic paint. The results were compared with traditional phosphate. The characterization of the coated samples was performed using tests of adhesion to verify the adherence of the pre-coating the ink-substrate. The salt spray test was performed to compare the resistance of different coatings. The results show that alternative treatments have good adhesion properties and corrosion resistance. The use of environmentally friendly coatings is viable because they have protection against corrosion, and it seems comparable to that observed for the phosphate.

Key words: Pretreatment; Conversion coatings; Nanoceramic.

COMPARAÇÃO DO DESEMPENHO DE PRÉ-REVESTIMENTO PARA SUBSTITUIÇÃO DA FOSFATIZAÇÃO

Resumo

A proteção contra corrosão de estruturas metálicas através da aplicação de revestimentos orgânicos é obtida utilizando um complexo pré-tratamento antes da tinta. O pré-tratamento do metal, bem como primer, intermediário e top coat, são as camadas que compõem o sistema de proteção. Embora pré-tratamentos de cromato e fosfato sejam utilizados amplamente, os processos exigem soluções alternativas para a toxicidade do cromo e o efluente de lodo do fosfato e seus problemas ecológicos. Este fato ocasionou o desenvolvimento de novos pré-tratamentos livres de cromo e fosfato. Neste estudo, os novos pré-tratamentos à base de Zr e do complexo Zr e Ti foram aplicados a substratos de aço e revestidos com uma tinta orgânica. Os resultados foram comparados como fosfato tradicional. A caracterização foi realizada por testes de aderência, para verificar a adesão do pré-revestimento à tinta-substrato. O ensaio de névoa salina foi realizado para comparar a resistência dos diferentes revestimentos. Os resultados mostram que os tratamentos alternativos possuem boas propriedades de aderência e resistência à corrosão. A utilização destes revestimentos é viável dada à presença de pré-tratamentos ambientalmente amigáveis e o fato de possuem proteção contra a corrosão, e o que parece comparável ao observado quanto ao fosfatizado.

Palavras-chave: Pré-tratamento; Revestimento de conversão; Nanocerâmicos.

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1 INTRODUCTION

The metals get organic coating to improve the appearance and increase protection against corrosion. The performance of this coating is usually associated with application of a pre-treatment modifies the surface of the metal. The resulting pre-treatment improves the adhesion of the subsequent and reduces the tendency to result in corrosion.[(1)]
The phosphate has emerged as an economical and effective protection for metals exposed to many diverse applications and resources. Even today, phosphates, along with chromate have been presented as the most effective inhibitors for films preparation for painting steel and galvanized steel. Beyond efficiency, other reasons justifying the use of this treatment: good adhesion to the paint, good looks, thick and remarkable resistance to corrosion has been proven over many years of application. The main and perhaps sole argument for the replacement of the phosphate / chromate is his character pollutant.[(2)]
Although the conversion coatings based on phosphates and chromates are used over the years with efficiency, such as adding properties, good corrosion resistance and good adhesion to the ink, the need for new technologies, and with properties similar efficiency, but with processes ecologically sustainable.[(3)]
From this context, emerged a few lines of coatings free of chromium and phosphates, among them the nanoceramic. The nanoceramic is a product developed from chemical compounds based on hexafluorzirconium and / or hexafluortitanium acids for pretreatment of metal surfaces. From a conversion reaction is assumed to obtain an oxide layer on the surface of the metallic substrate. The coating has a great potential for substitution of phosphates which are already used for over 150 years in the pre-treatment of metals.
The main advantage of the coating nanoceramic and minimize waste in wastewater treatment from the process, since the process of phosphate has an effluent treatment is difficult when compared with the conversion process is a zirconium / titanium. The latter generates an aqueous effluent, with Ti and Zr ions.[(4)]
Among other advantages of this alternative is:

- The reduction of one step in the process, compared to phosphate, which can be observed compared in Figure 1 below.
- The decrease in energy expenditure, since the conversion coating is performed at room temperature, contrary to what occurs with traditional treatments of phosphate, which are conducted at elevated temperatures. This factor allows for energy savings during the process.
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Nanoreramic	Clean	Rinse	Conv. Coat.	Rinse	Rinse	
Fosfatização	Clean	Rinse	Conv. Coat.	Post – treat.	Rinse	Rinse

Figure 1 - Comparison of the nanoceramic coating process vs. phosphate coating.[(5)]

The manner of obtaining the conversion coatings is to convert the metal surface of a passive to active state, through the use of certain ions. The films can be formed consisting of a mixture of corrosion products between the metal substrate and the reduced ion species present in solution, forming a layer called "conversion coating". Can be obtained by simple immersion in a solution containing ions or application of cathodic current to the substrate to be coated by electrochemical deposition.[(6)]

In this paper, the study of surface treatment of steel SAE 1006, conversion solution using hexafluorzircônio acid based, a solution of hexafluorzircônio hexafluortitânio acid based and phosphate solution, associated with painting, corrosion protection . Studies were conducted in open circuit potential, scanning electron microscopy (SEM), grip tests and accelerated corrosion tests in salt spray, evaluating subcutaneous migration, degree of blistering and rusting.

2 MATERIAL AND METHODS

2.1 The Samples

The SAE 1006 steel with dimensions of 1x50x100mm passed by the following steps to prepare:

- Wash with detergent;
- Degreasing in alkaline degreasing 4% (Parco Cleaner 651 B) to 85 ° C for 300s;
- Washing with deionized water jets;
- Drying with compressed air at about 60 ° C.

4.2 Pré-tratamento Aplicado às Chapas de Aço Carbono

To form the conversion coating, steel was immersed in a solution of conversion by dip coat, using equipment Coating Deep Lift Disc 765-MA Marconi, sink rate for 7mm.s-1. After immersion, the plates remained in solution according to the established time at room temperature and were removed at the same speed. After removal, the plates were washed with deionized water and dried at 110 ° C for 10 minutes.

For comparison, uncoated plates were prepared for conversion, only degreased, called white (B), and plates treated with zinc phosphate, using the same cleaning procedure described above.

Pre-treated steel was painted with synthetic enamel paint commercial Standard White by dip coat speed immersion and withdrawal of 7mm.s-1, left to air dry for 48 hours and used after two weeks, to ensure complete cure of ink. This operation provides layers of paint of about 40μm.

2.3 Adhesion Test

The degree of adhesion of the paint layer on the substrate coated with a layer of conversion was measured according to ASTM D 3359. A grid containing 25 squares of 1x1mm was cut in the paint layer with the aid of a chisel. An adhesive tape (3M Scotch Tape 880 filaments) was adhered to the region with the grid and then detached. The degree of ink adhesion was a function of the area of detachment of the ink. Using this standard, the degree of compliance varies 5B (no detached area) to 0B (detached area greater than 65%)

2.4 Salt Spray Test

BASS held in camera brand to evaluate the protection offered by the layers of coated steel conversion and subsequent painting with enamel paint. The tests were conducted in accordance with ASTM B 117 to determine:

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2.4.1 Migration subcutaneous

For measure the degree of subcutaneous migration was made a number painted on the court, according to NBR MB 787-74 and the sample was introduced in salt spray.

2.4.2 Degree of rusting and blistering

The degree of rusting and blistering is described in Table 1, according to NBR 5770/84 and NBR 5841/74:

Tabela 1: Grau de enferrujamento e empolamento e suas respectivas Normas.

Rusting	NBR 5770/84	Degree of blistering	F0 (best) → F5
Blistering	NBR 5841/74	Bubble size	T0 (best) → T5
		Bubble density	D0 (best) → D5

2.5 Scanning Electron Microscopy (SEM)

To observe the morphology of the coatings, images were obtained on equipment scanning electron microscopy (SEM) and elemental analysis by energy dispersive spectroscopy (EDS), using a scanning electron microscope JEOL - JSM 5800, with a voltage of 20 KV.

3 RESULTS AND DISCUSSION

3.1 Adhesion Test

The adherence test showed that the adherence of the conversion coatings can be as good as promoted by adherence to the substrate phosphate and better than the substrate only degreased.

The substrate was degreased degree of adherence of 1B, with the highlighted area around 65%. For the coating obtained from solution conversion hexafluorzirconium acid based, as shown in the Figure 2, the conversion coating obtained during 30s in treatment had the highest degree of detachment, 2B, with about 25% of the test area. For the conversion coating obtained during the 60s and 120s, the region offset test is less than 5%, ie, the degree of adhesion corresponds to 4B and resembles the degree of adherence of the substrate phosphate. For the coating obtained from solution conversion hexafluorzirconium / titanium acid based, but can also be seen in the Figure 2, the coating showed the same degree of detachment, with areas of displaced approximate. These values are shown in Table 2.

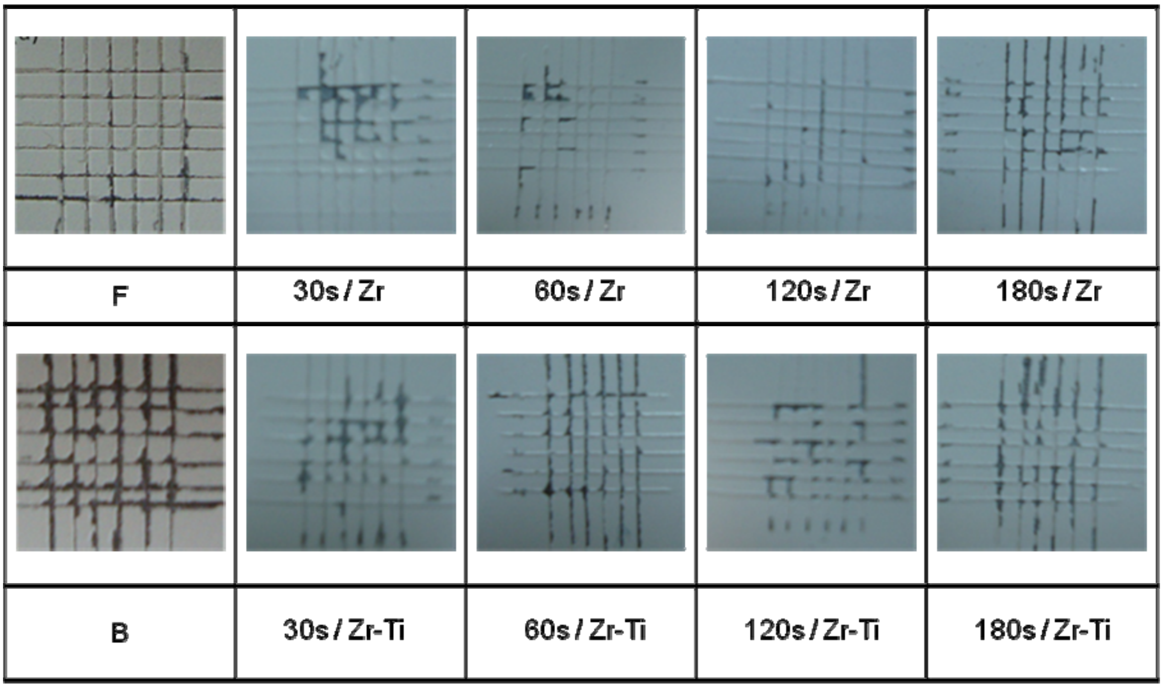

Figure 2. Visual observation of the steel samples coated with different pretreatments after adherence test.

Table 2 - Degree of adherence of the samples treated in bath solution based conversion according to ASTM 3359, compared with phosphate and without any pretreatment

Processing	t (s)	Degree of adherence	Area Offset
Zr	30	2B	~ 25%
Zr	60	4B	< 5%
Zr	120	4B	< 5%
Zr	180	3B	< 15%
Zr/Ti	30	3B	< 15%
Zr/Ti	60	3B	< 15%
Zr/Ti	120	3B	< 15%
Zr/Ti	180	3B	< 15%
Phosphating	-	4B	< 5%
Degrease	-	1B	~ 65%

3.2 Salt Spray Test

The salt spray results are presented in Table 3.
According to the results presented in Table 3 for the acid treatment hexafluorzirconium, those with better performance were subjected to 60s of treatment, since they are not rusting or blistering over 1488h salt spray, followed by conversion of the samples with 30s, which showed a minimal degree of rusting and blistering (F1, D1) in the period of 1488h. For the acid treatment hexafluorzirconium / titanium, the best performing samples was subjected to 30s of treatment, it did not present rusting or blistering over the 1032h.
Values in mm indicate the detachment of the coating from the cut made in the panel, after exposing the specimens to salt spray.

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Table 3 - Table 2: Results of salt spray: Degree of rusting and blistering and migration of the samples treated in solution of conversion, compared to phosphate and degreased

Processing	**t (s)**	**NSS (hr)**			**192 hr (mm)**
Zr	30	1488	F0	T1/D1	9.36
Zr	60	1488	F0	T0/D0	13.03
Zr	120	552	F0	T1/D1	11.46
Zr	180	552	F0	T1/D1	12.3
Zr/Ti	30	1032	F0	T0/D0	14.4
Zr/Ti	60	1032	F1	T2/D2	15.4
Zr/Ti	120	600	F1	T0/D0	13.15
Zr/Ti	180	600	F1	T0/D0	6.65
Phosphating	-	4B	F0	T0/D0	18,05
Degrease	-	96	F1	T3/D3	1.02

3.3 Scanning Electron Microscopy (SEM)

The microscopy showed the morphology of the substrates. The steel substrate phosphated showed crystals adhered on the surface, which contributes to corrosion protection and paint adhesion to the substrate, namely, its excellent performance as a pre-coating.

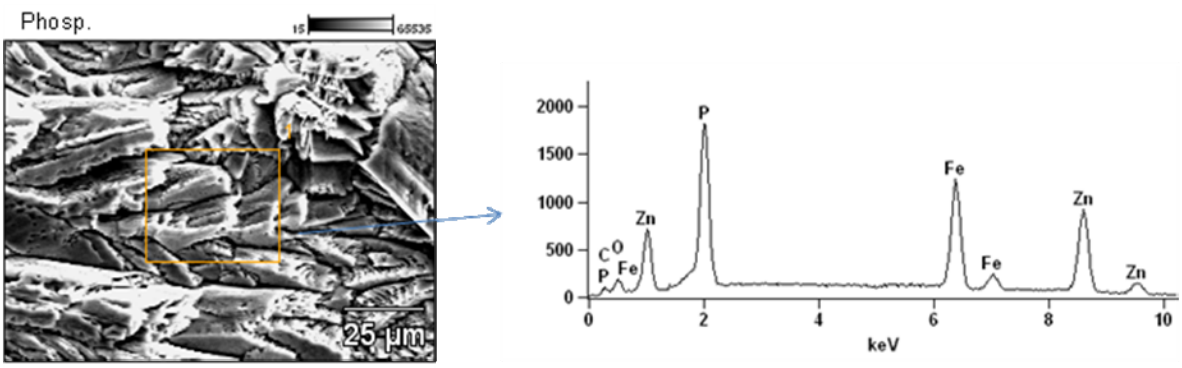

Figure 3. SEM / EDS of the sample that received coating based on zinc phosphate.

The steel substrate treated with conversion coating hexafluorzirconium acid based the complex hexafluorzirconium and hexafluortitânio acids has very similar morphology, but with the presence of titanium surface is lower than that of zirconium. In Figure 4 we notice in points (Point 1) greater than the presence of zirconium in steel matrix (field 2).

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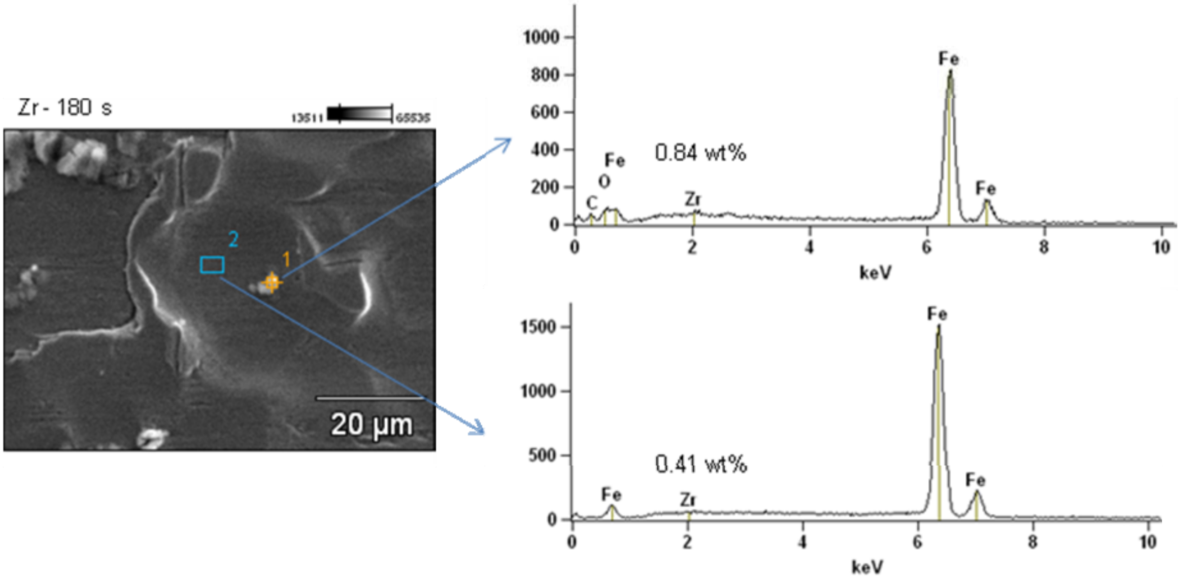

Figure 5. SEM / EDS of the sample that received hexafluorzirconium acid based coating, during the 180s in solution.

At lower magnification (250 microns), Figure 5, it is observed that the morphology of the layer thickness is low, without formation of crystals and the layer is deposited on a non-continues, but with the uniform presence zirconium (EDS), from the formation of zirconium oxide surface.

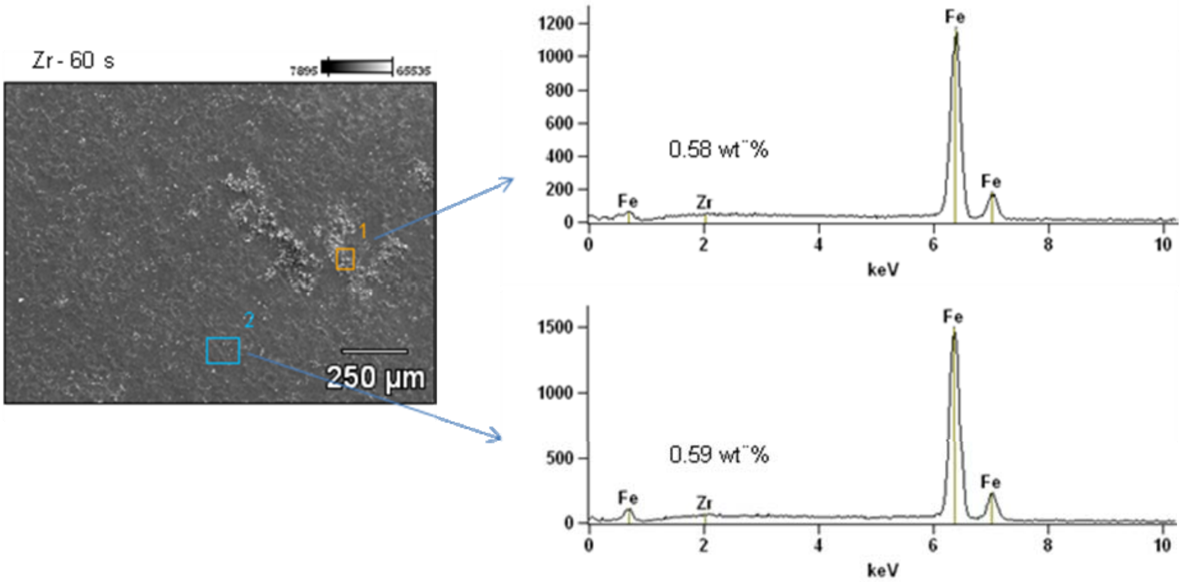

Figure 5. SEM / EDS of the sample that received hexafluorzirconium acid based coating, during the 120s in solution.

4 CONCLUSION

Comparatively, the processes studied have advantages and disadvantages between them. The process of phosphating is advantageous because it is an excellent adhesion promoter, due to the presence of crystals in this layer that favor the anchoring substrate-ink and his uniform and thick layer that helps as a barrier against corrosion. This factor always enshrined the zinc phosphate coating over the years. However, the increase in accuracy with respect to industrially discharged effluent has led to replacement of this process. The acid-based coating hexafluorzircônio promotes adherence to quantitatively paint as good as the phosphate coating in salt spray test for 1488h, the conversion coating obtained its best performance when used for a period of 60s, also obtained by coating performance phosphate. However, below the substrate phosphate was obtained for the migration test, the same happens with the coating hexafluorzirconium / titanium acid based, which apparently has underperformed coating hexafluorzirconium acid based, however, had a time of 1032h salt spray. These new treatments conversion processes tend to replace phosphate in some production lines, since they have the advantage of wastewater treatment, energy economy and its performance coating to protect against corrosion.

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REFERENCES

1 DECK, P., MOON, M., SUJDAK, R. Investigation of fluoacid based conversion coatings on aluminum. Progress in Organic Coatings. v. 34, 39–48, 1998.
2 LUNDER, O., SIMENSEN, C., YU, Y., NISANCIOGLU, K. Formation and characterization of Ti–Zr based conversion layers on AA6060 Aluminium. Surface and Coatings Technology. v.184, p. 278–29, 2004.
3 PANOSSIAN, Z., Curso de fosfatização de Metais Ferrosos. ABM. São Paulo, 2004
4 ZAPAROLLI D., Químicas e derivados on-line, editor QD LTDA, edição 439, tratamento de superfície. Disponível em: <http://www.quimica.com.br/revista/qd439/tratamento_de_superficie1.html> Química e Derivados Edição nº 439 de Julho 2005.
5 FRISTAD, W., An Environmentally Friendly Non-PhosphateConversion Coating, US PITTURE E VERNICI - EUROPEAN COATINGS 2006.
6 WILCOX, G. D., GABE, D. R., WARWICK, M. E., Chemical molybdate conversion treatments for zinc. Metal Finishing, v. 86, n. 9, p. 71 – 71, 1998.