


# Corrosion Resistance of Unlacquered Chromium-Plated Steel Sheets – Study on the Influence of Pickling and Chemical Treatment Steps of the Production Process

Alessandro D. Oliveira<sup>a,c</sup>, Gabriel F. Bettencourt<sup>b,c</sup>, João L.C. Santos<sup>a</sup>,  
Daniela F.G. de Jesus<sup>c</sup>, Tatiana C. Almeida<sup>c\*</sup> 

<sup>a</sup>Companhia Siderúrgica Nacional, Centro de Pesquisa, Volta Redonda, RJ, Brasil.

<sup>b</sup>Companhia Siderúrgica Nacional, Gerência de Estanhamento Eletrolítico, Volta Redonda, RJ, Brasil.

<sup>c</sup>Universidade Federal Fluminense, Escola de Engenharia Industrial Metalúrgica, Volta Redonda, RJ, Brasil.

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The corrosion resistance of chromium-plated steel sheets produced on an industrial scale was investigated. Two parameters of the production process were considered: pickling and chemical treatment. The specimens were produced at the industrial plant considering two different pickling conditions and two different chemical treatments: non-electrolytic and electrolytic pickling and non-electrolytic and electrolytic passivation respectively. Accelerated corrosion tests in the humid chamber, microscopy analyses, analyses of roughness and content of trivalent chromium in the passivation film and analyses of the content of metallic chromium in the coating by coulometry technique were performed. The results showed a low corrosion resistance of the materials produced with the non-electrolytic passivation, regardless of the pickling condition. The highest degree of protection of the base steel was achieved for the specimen produced by using the electrolytic route for both pickling and chemical treatment steps. This condition produced a mass of trivalent chromium in the passivation film greater than  $8.0 \text{ mg} \cdot \text{m}^{-2}$ , which provided an effective performance of the chromium-plated steel sheet.

**Keywords:** Corrosion Resistance, Unlacquered Chromium-Plated Steel, Pickling, Chemical Treatment.

## 1. Introduction

Chromium-plated steel sheets, also known as electrolytic chromium coated steel (ECCS) arose in the 1960s as an alternative to tinplate for the production of steel packaging for food and chemicals<sup>1,2</sup>. In practice, chromium-plated steel sheets have successfully replaced tinplate, especially in the manufacture of lids and bottoms of packages, as well as in the production of drawn two-piece cans. Some of the positive points of ECCS are the lower cost, compared to tinplate, the greater resistance to high temperatures and the excellent adhesion of organic coatings<sup>1-4</sup>.

The continuous process of producing chromium-plated steel sheets involves the following main steps: steel surface pretreatment (alkaline cleaning and acid pickling), metallic chromium electrodeposition followed by a chemical treatment or passivation of this coating (deposition of a chromium oxide/hydroxide film) from baths based on chromic acid. As a last step, the application of a thin film of a lubricating oil on the surface of the material is performed to minimize damage from abrasion. Thus, the protection of the base steel in ECCS is related to the thin electrodeposited layer of metallic chromium and the passivation film based on trivalent chromium compounds<sup>1,5</sup>.

It should be highlighted that most of the ECCS produced in the world is still based on hexavalent chromium baths. This occurs despite the growing effort of the scientific community

in recent years to search for more suitable alternatives from an environmental and public health point of view<sup>6-8</sup>.

The chromium layer on the chromium-plated steel sheets acts as a cathodic coating, protecting the base steel through a barrier effect<sup>2</sup>. This protection mechanism and the small thickness of the coating (ranging from 10 nm to 20 nm) are factors that justify the frequent necessity to lacquer the material. However, in general, the time elapsed between the production of ECCS at steel mill and the process of lacquering the material in the producers of steel packaging can involve a few weeks or months. In this context, there is a great concern to control the development of iron oxides during this storage period of the chromium-plated steel coils, to ensure the success of the entire production chain involved.

The acid pickling and chemical treatment stages of the ECCS production process play a fundamental role in controlling the development of iron oxides in the period between the production of the chromium-plated steel coils and their lacquering<sup>9-12</sup>. At first, the more effective the pickling, the better the quality of the metallic chromium deposit<sup>1,2</sup>. On the other hand, the chromium oxide/hydroxide from the passivation film is supposed to be a sealing agent for the porosity of the metallic chromium coating, minimizing exposure of the base steel. The greater the mass of trivalent chromium in this passivation film, the greater the corrosion resistance of the chromium-plated steel sheets<sup>5</sup>. However, very high values of trivalent chromium can cause problems

\*e-mail: [tatianachagas@id.uff.br](mailto:tatianachagas@id.uff.br)

with the visual aspect of the material, due to the appearance of stains. Regarding the minimum mass of chromium in the passivation film, to guarantee a suitable corrosion resistance, the literature<sup>1,13-15</sup> points out different values, ranging from 5.0 mg·m<sup>-2</sup> to 8.0 mg·m<sup>-2</sup>.

Despite the existence of a consensus regarding the importance of the pickling and chemical treatment steps in the quality of chromium-plated steel sheets, there is a lack of dissemination of data obtained industrially by the steel mills in the literature. The aim of the present work was to investigate, on an industrial scale, the influence of pickling and chemical treatment on the corrosion resistance of unlacquered chromium-plated steel sheets.

## 2. Experimental Development

### 2.1. Specimens production

The chromium-plated steel specimens were produced at an industrial plant from two carbon steel coils with chemical composition shown in Table 1.

The process parameters used in the different stages of the chromium electrodeposition line were within the working ranges established by the company's standards, except for the pickling and chemical treatment stages, where the experiments were carried out. The electrical parameters regarding per strip side in these two steps are shown in Table 2, which are non-electrolytic pickling (NEP), electrolytic pickling (EP), non-electrolytic chemical treatment (NET) and electrolytic chemical treatment (ET) combined among them. The specimens were named by abbreviations of pickling and chemical treatment conditions.

### 2.2. Specimens characterization and performance evaluation

The characterization of the specimens surface involved the analyses of roughness, content of metallic chromium in the coating and content of trivalent chromium (as oxide/hydroxide) on the passivation film. The performance of the specimens regarding the protection of the base steel against corrosion was determined through an accelerated wet

chamber exposure test and through microscopic analysis. The specimens were analyzed at least in triplicate for all the tests.

The roughness (Ra parameter) was measured using a Mitutoyo roughness meter, model SJ-301 and "cut off" parameter of 0.8 x 5 mm.

The mass of metallic chromium in the coating was determined by the coulometric technique of anodic dissolution in sodium diacid phosphate solution, according to ABNT NBR 15376<sup>16</sup>. In this analysis an Omnimetra Instruments potentiostat/galvanostat model PG-3901 and a conventional three-electrode electrochemical cell were used (working electrode: chrome plated steel sheet; auxiliary electrode: platinum spiral; reference electrode: calomel 1M).

The mass of trivalent chromium on the passivation film was quantified by using a colorimetric technique, in accordance with EN 10202<sup>13</sup> and ABNT NBR 8750<sup>17</sup> standards.

The exposure test in a humid chamber (100% relative humidity and temperature of 40 °C) was carried out with 20 cm x 15 cm panels in triplicates for each type of specimen. The comparative evaluation was performed by visual analysis (naked eye), after 7 days of exposure in the chamber. However, some panels were exposed for up to 47 days to verify the evolution of the corrosive process.

The microscopic evaluation of the specimens produced in the chromium plating line was carried out after 22 days and 180 days of storage at room temperature. Backscattered electron images and energy dispersive X-ray microanalyses (EDS) were performed using a scanning electron microscope (SEM) of FEI Company, model Quanta 3D FEG.

## 3. Results and Discussion

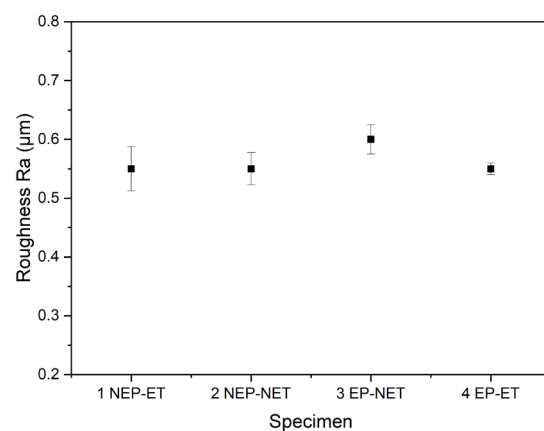
Figures 1 and 2 show the results of the analyses of the roughness and mass of metallic chromium on the surface of the specimens. The roughness values (Figure 1) are in accordance with the "stone" specification (0,35 µm to 0,60 µm), according to the ABNT NBR6665<sup>14</sup> standard. No significant difference due to variations in the pickling and chemical treatment conditions were observed. The masses of metallic chromium (Figure 2) were also at the same levels, with all the values exceeding the minimum limit established in the standard (30 mg·m<sup>-2</sup>).

**Table 1.** Chemical composition of the steel used for the production of the chromium-plated specimens.

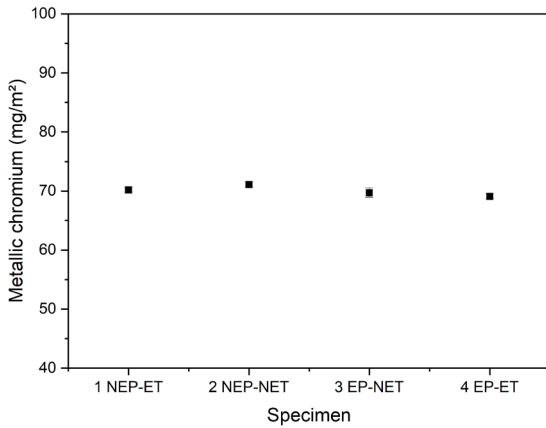
Maximum Level (% w/w)									
C	Si	Mn	S	Cu	P	Ni	Al	Cr	Others, each
0.13	0.03	0.60	0.03	0.20	0.03	0.01	0.08	0.10	0.02

**Table 2.** Process electrical parameters of the pickling and chemical treatment stages used for the industrial production of chromium-plated steel sheets; the range of line speed was 250 to 300 m·min<sup>-1</sup>.

Specimen	Pickling		Chemical Treatment
	Electric Current (A)	Electric Current (A)	Average Density of Cathodic Electric Charge (C·dm <sup>-2</sup> )
1 NEP-ET	Zero	2500 to 3000	7.5
2 NEP-NET	Zero	Zero	Zero
3 EP-NET	2200 to 2700	Zero	Zero
4 EP-ET	2200 to 2700	2500 to 3000	7.5

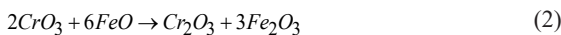
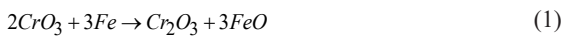


**Figure 1.** Roughness of the specimens (Ra parameter), the abbreviations mean: NEP - non-electrolytic pickling, EP - electrolytic pickling, NET - non-electrolytic chemical treatment and ET - electrolytic chemical treatment.



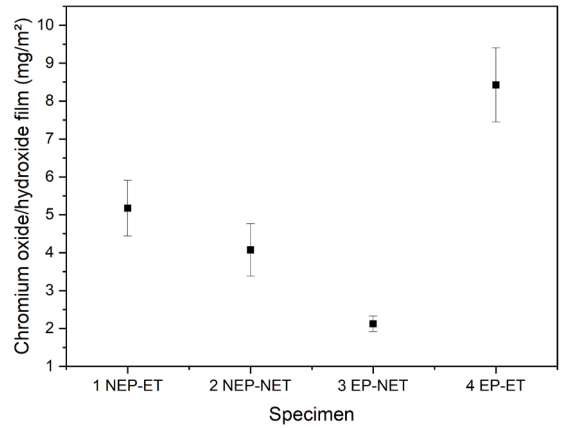
**Figure 2.** Metallic chromium in the coating of the specimens, the abbreviations mean: NEP - non-electrolytic pickling, EP - electrolytic pickling, NET - non-electrolytic chemical treatment and ET - electrolytic chemical treatment.

The results obtained in the analyses of the mass of trivalent chromium in the passivation film of the specimens are shown in Figure 3. The lowest values for the chromium film were reached for the case of non-electrolytic chemical treatment (specimens 2 NEP-NET and 3 EP-NET, with mean values of 4.0 mg·m<sup>-2</sup> and 2.1 mg·m<sup>-2</sup>, respectively). It can also be seen that between these two specimens, the one processed with non-electrolytic pickling (specimen 2 NEP-NET) showed a higher value. The hypothesis that could explain this fact is that a less active pickling condition tends to provide metallic chromium deposits with a higher level of porosity (higher level of iron exposure). On the other hand, for the non-electrolytic chemical treatment, the mechanism of reduction of the hexavalent chromium in the passivation bath, to generate the trivalent chromium oxide/hydroxide film, involves a redox reaction. This reaction is intensified by the metallic iron or ferrous oxide exposed into the pores of the metallic chromium coating. The following chemical equations are representative of this overall process:



According to this interpretation, the greater porosity of the metallic chromium coating produced using non-electrolytic pickling of the base steel would enable greater deposition of the trivalent chromium in the non-electrolytic chemical treatment step.

In Figure 3 is also verified that for the electrolytic chemical treatment, the highest mass of trivalent chromium on the passivation film was obtained for the specimen 4 EP-ET (8.4 mg·m<sup>-2</sup>), processed with electrolytic pickling. For specimen 1 NEP-ET, produced with non-electrolytic pickling, this mass was at a lower level (5.2 mg·m<sup>-2</sup>). This behavior may be related to the fact that in the case of electrolytic chemical treatment, the iron oxides on the surface, even at a microscopic level, can consume a fraction of the cathodic current applied for the formation of the chromium oxide/



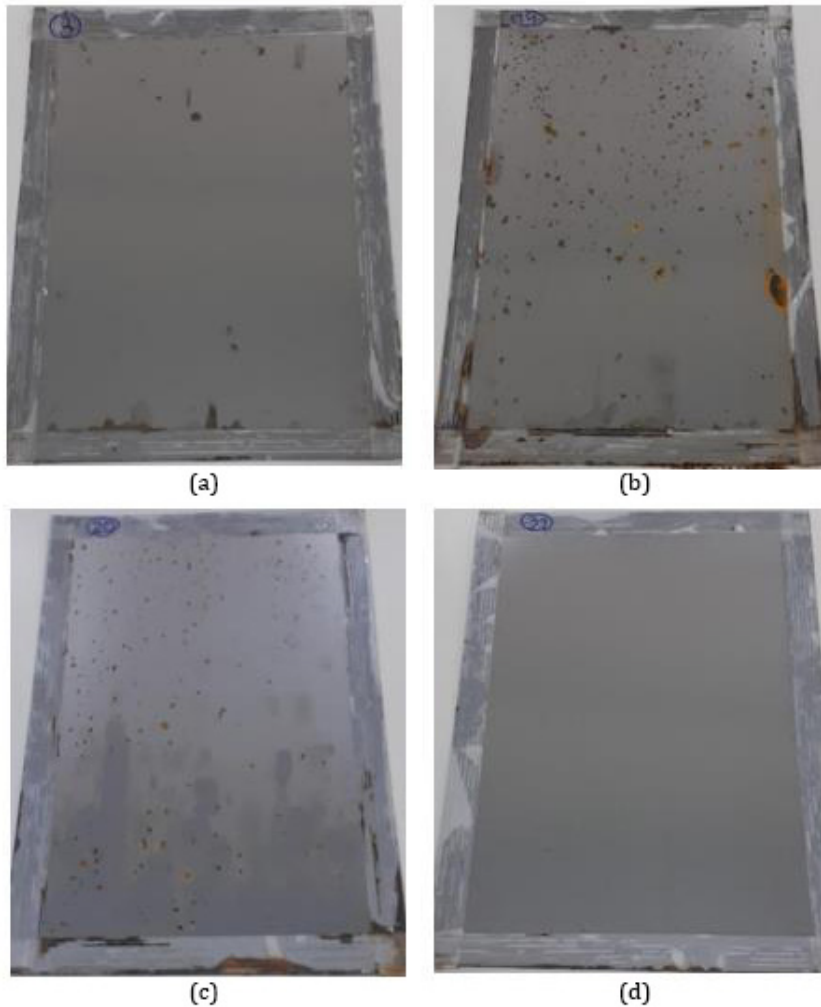
**Figure 3.** Trivalent chromium in the passivation film of the specimens, the abbreviations mean: NEP - non-electrolytic pickling, EP - electrolytic pickling, NET - non-electrolytic chemical treatment and ET - electrolytic chemical treatment.

hydroxide film. Thus, specimen 1 NEP-ET would be more susceptible to this phenomenon.

Some studies showed the effect of pickling on electroplating<sup>9-12</sup>. However, without applying electrolytic pickling, parameter that was evaluate in this study. Guan et al.<sup>10</sup> showed that the porosity for the electroplating increased abruptly after an overpickling. In the Hyie et al.<sup>9</sup> study, the surface pre-treatment using sulfuric acid had shown good results at a 10 vol% concentration of sulfuric acid and 60 seconds of immersion. Uniform plating with better hardness without peeling, pitting, and cracking was observed by the authors. Herein, in addition to acid pickling, the chemical treatment (electrolytic or not) showed an important role in the chromium-plated steel, as seen in Figure 3.

The performance of the specimens in the wet chamber test was expressed through the visual analysis of the panels after 7 days of exposure. The following increasing order of corrosion resistance of the base steel was obtained: specimen 2 NEP-NET = specimen 3 EP-NET < specimen 1 NEP-ET < specimen 4 EP-ET. Thus, it was observed that specimens 2 NEP-NET and 3 EP-NET, processed with non-electrolytic chemical treatment, showed the largest extent of corrosive attack, with no influence of pickling conditions. For specimens processed with electrolytic chemical treatment, it was verified that the one produced with the non-electrolytic pickling (specimen 1 NEP-ET) presented an intermediate extent of corrosive attack. Lastly, specimen 4 EP-ET, produced with electrolytic pickling and electrolytic chemical treatment, did not show visible signs of corrosion after 7 days of testing. Figure 4 presents a photograph of a representative panel of the triplicates, for each one of the four specimens, showing the extent of the corrosion.

The greater corrosion resistance of specimen 4 EP-ET can also be seen after 47 days of exposure in the humid chamber. Even after this long test period, there was no significant development of corrosive processes on the surface of the material, as shown in Figure 5. It is worth mentioning that this specimen was the one that presented the highest mass of chromium oxide/hydroxide in the passivation



**Figure 4.** Photographs of representative panels of the triplicates, for each of the four specimens, after 7 days of exposure in the humid chamber test. Specimens (a) 1 NEP-ET, (b) 2 NEP-NET, (c) 3 EP-NET and (d) 4 EP-ET. The abbreviations mean: NEP - non-electrolytic pickling, EP - electrolytic pickling, NET - non-electrolytic chemical treatment and ET - electrolytic chemical treatment.

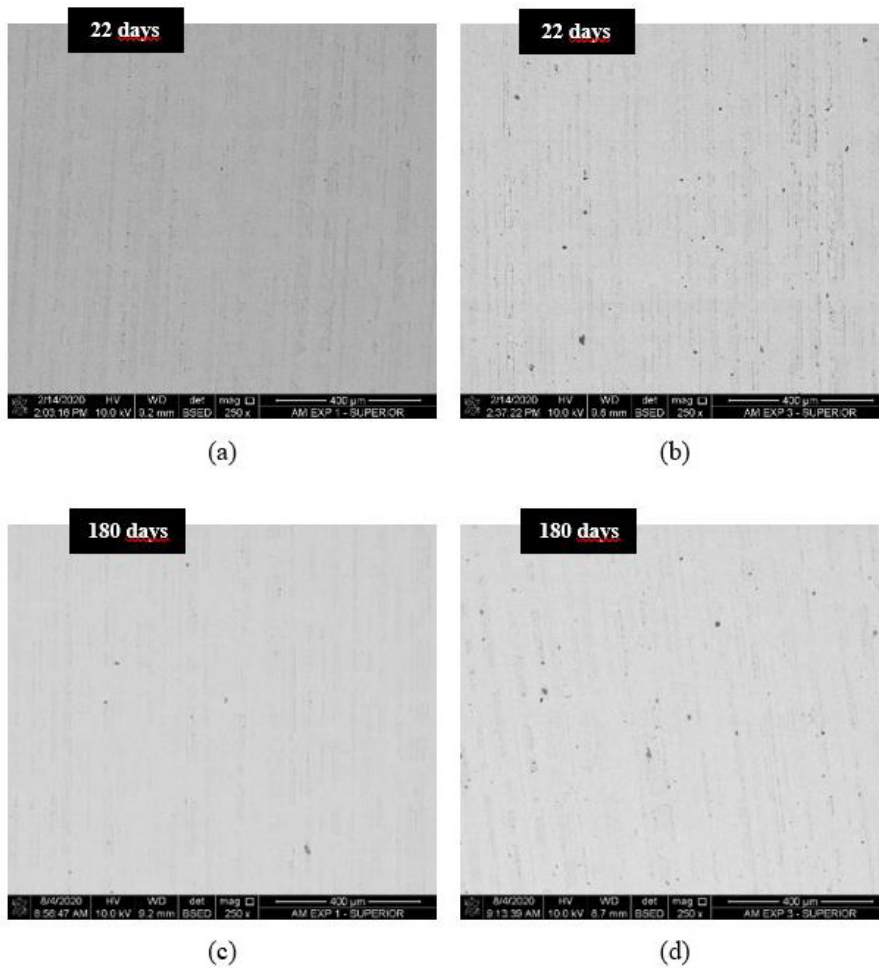


**Figure 5.** Photograph of a representative panel of specimen 4 EP-ET, after 47 days of exposure in the humid chamber test. The abbreviation EP-ET means electrolytic pickling and electrolytic chemical treatment respectively.

film ( $8.4 \text{ mg}\cdot\text{m}^{-2}$ ). This superior performance of specimen 4 EP-ET in protecting the base steel confirms the importance of trivalent chromium mass in the passivation film of the material. It is also clear that levels of trivalent chromium in the range of  $5.0 \text{ mg}\cdot\text{m}^{-2}$  (specimen 1 NEP-ET) may not be enough to guarantee the protection of the base steel of the unlacquered chromium-plated steel sheets.

Figure 6 shows images of backscattered electrons obtained by SEM for the specimens produced in the chromium plating line with non-electrolytic pickling, after 22 days and 180 days of storage at room temperature. It is worth saying that each specimen was analyzed in different regions, which were similar to each other. Thus, the results represent the macroscopic behavior of the materials.

Figure 6a shows that after 22 days of production, no significant corrosion spots were evident on the surface of the specimen 1 NEP-ET (produced with non-electrolytic pickling and electrolytic chemical treatment). However, after 180 days of production, this specimen exhibited dark spots on the surface, associated with the development of iron oxides



**Figure 6.** Images by SEM-BSED for specimens (a, c) 1 NEP-ET and (b, d) 2 NEP-NET after 22 days and 180 days of storage at room temperature. The abbreviations mean: NEP - non-electrolytic pickling, NET - non-electrolytic chemical treatment and ET - electrolytic chemical treatment.

(Figure 6c). Figure 6 also shows that for specimen 2 NEP-NET (produced with non-electrolytic pickling and non-electrolytic chemical treatment), the spots of iron oxides were already observed even after only 22 days of production (Figure 6b). For this specimen, the increase in storage time apparently did not result in a significant increase in the extent of the corrosion, as seen for the period of 180 days (Figure 6d).

Figure 7 presents an image of backscattered electrons with higher magnification, of the surface of specimen 2 NEP-NET, after 180 days of production. In this image, points 1 and 2 were marked. The microanalyses that were carried out in these points confirmed that the dark spots are really iron oxides (presence of a high intensity peak of the element oxygen at the point 2). This same behavior was obtained for all the other specimens, whose backscattered electron images revealed dark spots on the surface.

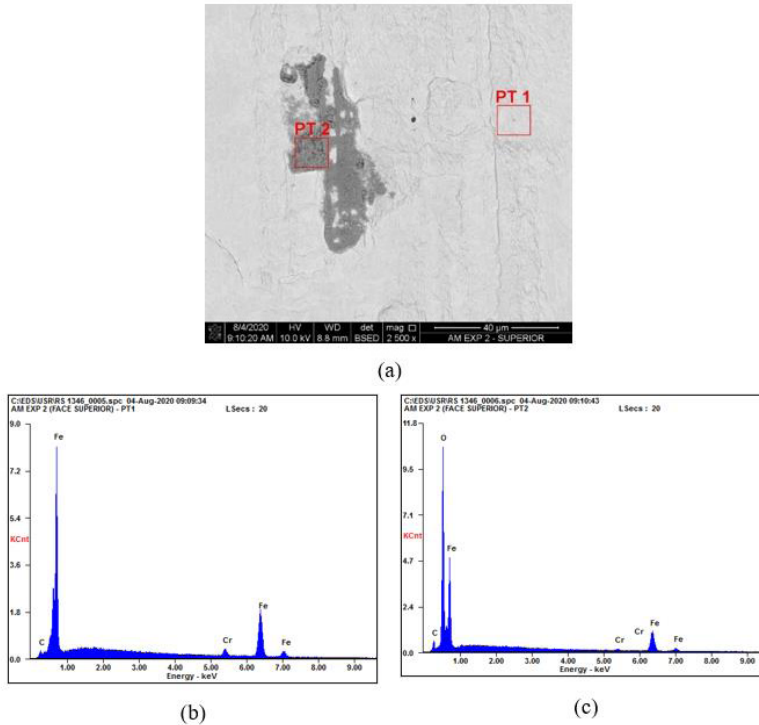
Figure 8 shows the images of backscattered electrons recorded for the specimens processed in the chromium plating line with electrolytic pickling, after 22 days and 180 days of storage at room temperature. The specimen 3 EP-NET, produced with electrolytic pickling and non-electrolytic

chemical treatment, showed dark spots on the surface after 22 days of storage (Figure 8a), with no significant increase of this characteristic over time, as shown in the image for 180 days (Figure 8c). This behavior was similar to that verified for specimen 2 (produced with non-electrolytic process for pickling and chemical treatment, Figure 6b and 6d). Figure 8 also shows that for specimen 4 EP-ET, produced with electrolytic pickling and electrolytic chemical treatment, no corrosive attack was observed, even after 180 days of storage (Figure 8b and 8d).

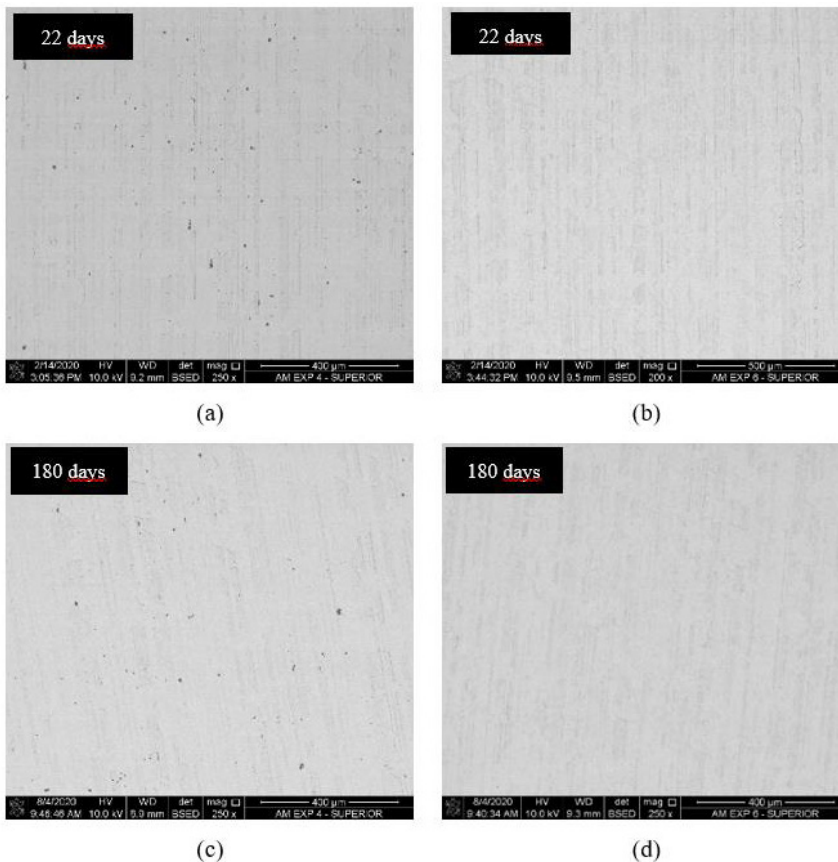
#### 4. Conclusions

The global analysis of the results shows that the specimens produced in the industrial chromium plating line presented equivalent values for roughness and metallic chromium coating. Both parameters were within the specification limits:  $0.30\ \mu\text{m}$  to  $0.60\ \mu\text{m}$  and  $30\ \text{mg}\cdot\text{m}^{-2}$  (minimum), respectively, regardless of pickling and chemical treatment conditions.

This work ratified the importance of the chromium oxide/hydroxide film in the corrosion resistance of chromium-



**Figure 7.** Image by (a) SEM-BSED for specimen 2 NEP-NET after 180 days of production and EDS at the points (b) 1 and (c) 2. The abbreviation NEP-NET means non-electrolytic pickling and non-electrolytic chemical treatment respectively.



**Figure 8.** Images by SEM-EBSD for specimens (a, c) 3 EP-NET and (b, d) 4 EP-ET after 22 days and 180 days of storage at room temperature. The abbreviations mean: EP - electrolytic pickling, NET - non-electrolytic chemical treatment and ET - electrolytic chemical treatment.

plated steel sheets. Specimens 2 and 3, produced with non-electrolytic chemical treatment, showed the lowest contents of trivalent chromium in the passivation film, which were not enough to ensure efficient sealing of the pores of the metallic chromium coating. This fact was highlighted by the accelerated test of exposure in a humid chamber and by the microscopic analysis of the specimens stored at room temperature for 22 days and 180 days. In both evaluations, the corrosion of the base steel was clearly evidenced for these specimens.

The use of electrolytic chemical treatment (average electrical charge density of  $7.5 \text{ C}\cdot\text{dm}^{-2}$ ) enabled the production of chromium-plated steel sheets with greater resistance to corrosion. In this situation, the influence of the pickling step on the performance of the materials was clear. Specimen 1, processed with non-electrolytic pickling, showed a mass of chromium oxide/hydroxide in the passivation film of  $5.2 \text{ mg}\cdot\text{m}^{-2}$  and a lower corrosion resistance than specimen 4, processed with electrolytic pickling. The better corrosion resistance of specimen 4 is associated with a mass of trivalent chromium in the passivation film greater than  $8.0 \text{ mg}\cdot\text{m}^{-2}$ .

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