Hopeite-type phosphate coatings in which zinc is partially replaced by other metals like manganese and nickel are of great interest for the automotive and home appliance industries. Such industries use phosphate conversion coatings on galvanized steels in association with cataphoretic electropainting. Zinc phosphates modified with manganese and nickel are isomorphic with the hopeite, and the phase identification using X-ray diffraction is difficult. In this paper, the phosphate coatings are identified using the Fourier transform infrared spectroscopy (FTIR).

Keywords: Surfaces, zinc phosphate, coatings, infrared spectroscopy.

1. Introduction

The phosphating process is widely used by the industry as a pre-treatment of metallic surfaces before painting, promoting the paint adherence and protecting the substrate against corrosion.

Zinc phosphate coatings on steel consist mainly of crystalline α-hopeite, orthorhombic α-[Zn₃(PO₄)₂·4H₂O] and crystalline phosphophyllite [Zn₂Fe(PO₄)₂·4H₂O] (Pawlig & Trettin, 1999). The relative amount of these two phases is a widely used parameter for the evaluation of the...
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In the present work, Fourier transform infrared spectroscopy (FTIR) was used for the analysis of phosphate layers produced from phosphating solutions with different chemical compositions.

2. Experimental

The electrogalvanized steel sheet was produced by Usinmas Steel Works (Alvarenga et al., 1994) and the phosphating of the samples was performed at the laboratory of Henk Surface Technologies Brasil Ltda., by immersion in phosphating baths with the compositions presented in Table 1.

In the phosphating process the samples were degreased with a 3 wt.% solution of the product Parco Cleaner 1522 AV at 333 K, and rinsed with water (Fernandes, 2002). The samples were then immerged in a bath containing 1 g/L of the titanium-based refiner Fixodine 18 for 30 s at the temperature of 333 K. Refiner is used to prepare the metallic surface for the nucleation and growth of the phosphate crystals. In the next step the samples were immerged in the phosphating solution for 1 minute at the temperature of 333 K and rinsed with running water and dried at 373 K for 2 minutes. This procedure was used for each of the phosphating baths shown in Table 1.

The samples were weighed in an analytical balance with a precision of 0.1 mg. The phosphate layer was removed by immersing each sample in a solution of CrO3 (0.5% w/v at 343 K) for 5 minutes. The samples were then rinsed with distilled water, dried and weighed again.

The solution used for the removal of the phosphate coating on each sample was calibrated and then analyzed by atomic absorption spectroscopy for the determination of the elements present in the coating. The equipment used was an Inductive Coupled Plasma Spectrometer -Spectroflame Modula.

The morphology of the phosphate coating was characterized by scanning electron microscopy (SEM) using a Stereoscan 360/Cambridge microscope.

The analyses by Fourier transform infrared spectroscopy (FTIR) were performed with a Perkin-Elmer Paragon-1000 FTIR Spectrometer, using the specular reflectance accessory with a fixed angle of incidence of 16°, spectral resolution of 2 cm⁻¹ and the average of 32 single scans. The result obtained using this technique is the same as that obtained using transmission in a film self-supported film with double thickness, and the results are shown as transmission values.

The phosphated samples were heat-treated and analyzed again using the same Fourier transform infrared spectroscopy technique. The objective of the heat treatment was to verify the changes, which could take place in the coatings, such as partial or total dehydration, as well as to aid the identification of the phases present in the phosphate coating. The heat treatment was performed in a drying and sterilizing oven Fanem model 920SE - Mechanical Circulation, during 1 hour, at 393 K for samples E-F2 and E-F4, 413 K for samples E-F1 and E-F3 and 453 K for the sample E-F5.

3. Results and discussion

The results in Table 2 show that the mass of the phosphate coating varied according to the composition of the phosphating bath. Sample E-F1, a tricationic phosphate layer on electrogalvanized steel, showed the highest phosphate coating mass while the lowest mass corresponded to the Zn/Mn phosphate layer on zinc coated steel. Manganese has a lower molecular mass than zinc and nickel, the other elements that constitute the phosphate layer. This variation was attributed to the chemical reactivity of each phosphating bath. The structure of inorganic phosphate coatings depends on their film

| Identification of the samples | Type of coating formed | Chemical composition of the bath (g/L) | Acidity (mL NaOH 0.1N) |
|-------------------------------|------------------------|--------------------------------------|-----------------------|
| E-F1                          | tri-cation             | 1.18 0.73 0.68                      | 0.50 18.0             |
| E-F2                          | pure hopeite           | 1.23 - -                             | 0.50 17.9             |
| E-F3                          | Mn-modified hopeite    | 1.15 0.80 -                          | 0.60 17.9             |
| E-F4                          | Ni-modified hopeite (low content) | 1.16 - 0.43 | 0.50 17.8 |
| E-F5                          | Ni-modified hopeite (high content) | 1.16 - 0.86 | 0.60 17.9 |

Table 1: Chemical composition of the baths used in the phosphating of electrogalvanized steels.
weight (Weng et al., 1996). Middle-weight (1.4 - 7.5 g/m²) as well as heavy-weight (7.5 - 30 g/m²) phosphate film demonstrates a crystal structure (Weng et al, 1996). The phosphate coatings studied can be classified as middle-weight according to Table 2. The phosphate crystals were fine, compact and had the shape of platelets, uniformly covering the surface of the samples. No significant differences were observed between the phosphate coatings for the samples investigated. Fedrizi et al. (2001) related that the main difference between the zinc phosphate and the tri-cation phosphate appears to be the phosphate crystal size, which is much smaller in the case of the tri-cation phosphate process.

Figure 1 shows an infrared spectrum representative of the phosphate coating of sample E-F2 (pure hopeite).

According to the results given in Table 3 the phosphate coatings show several bands with strong absorption between 1200 cm⁻¹ and 900 cm⁻¹ in the spectrum. The spectra show characteristic absorptions due to the PO₄³⁻ group (ν₁: 929 cm⁻¹, ν₂: 1105, 1066, 1026, and 1000 cm⁻¹, ν₃: 635 cm⁻¹). These results confirm the observations by Molt et al. (1994) and Pawlig and Trettin (1999).

In addition, water bending (1639 cm⁻¹) and OH stretching (3546 cm⁻¹) and a broad band centered at 3300-3400 cm⁻¹ vibrations can be observed (Figure 1 and Table 3). Their positions are consistent with the presence of a hydrogen-bonding network within the crystal lattice. However, the sharp band at 3546 cm⁻¹ indicates that some OH groups do not participate in hydrogen bonding. Frost (2004) identified four infrared bands of the hydroxyl stretching region of hopeite, which are at 3542, 3473, 3338, and 3149 cm⁻¹. Pawling et al (2001) reported the infrared spectrum of hopeite and its deuteron-analogs. They reported infrared bands at 3537, 3410, 3263, and 3181 cm⁻¹. The structure of hopeite consists of ZnO₂(H₂O)₄ octahedra, ZnO₄ tetrahedra, and PO₄ tetrahedra, none of which are regular, these polyhedra share corners and edges (Whitaker, 1975). It is likely that the two water molecules are non-equivalent, thus giving rise to in-phase and out-of-phase behavior. Hence, two infrared bands would be expected. In this work, two infrared bands of the hydroxyl stretching region of hopeite are observed, at 3510 and 3265 cm⁻¹ (Table 3).

The numerous bands in the phosphate region can be explained by the low C₁ site symmetry of the phosphate ion in the hopeite structure. Hopeite (EF-2) showed three intense bands: a single band...
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at 935 cm\(^{-1}\) and two doublets at 1019 cm\(^{-1}\)/1000 cm\(^{-1}\) and 1104 cm\(^{-1} \)/1067 cm\(^{-1}\), Table 3 and Figure 2. The bands at 1019, 1000, 1104 and 1067 cm\(^{-1}\) are assigned to the \(\nu_3\) PO\(_4\) antisymmetric stretching modes (Frost, 2004). The band at 935 cm\(^{-1}\) is ascribed to the \(\nu_1\) symmetric stretching modes. Frost (2004) identified bands at 1137, 1096, 1059, 1019, 995 cm\(^{-1}\), which are assigned to the \(\nu_3\) PO\(_4\) antisymmetric stretching modes (Frost, 2004), and bands at 945 and 922 cm\(^{-1}\) ascribed to the \(\nu_1\) symmetric stretching modes, in the hopeite infrared spectrum. Molt et al. (1994) identified only one doublet for pure hopeite at 1099 cm\(^{-1}\)/1070 cm\(^{-1}\) and also reported an additional band at 1020 cm\(^{-1}\) for the compounds derived from the hopeite with manganese and/or nickel, which has not been observed in the present work, according to the results shown in Table 3.

Table 4 shows the position of the bands in the infrared spectra of phosphate coatings after heat treatment.

As can be seen in Table 4 the partial dehydration of the phosphate coatings start at 393 K for the samples E-F2 and E-F4.

The \(\nu\)OH vibration peak, around 3500 cm\(^{-1}\), disappears at 393 K for the hopeite (sample E-F2). Pawlig and Trettin (1999) reported that when a heating rate of 5 or 10 K/min was used, the dehydration of \(\alpha\)-hopeite was accompanied by three endothermic effects. The onset temperatures were 374, 411, and 542 K for a heating rate of 10 k/min and 363, 410, and 535 K for a heating rate of 5 K/min. Pawlig and Trettin (1999) observed that the first and second endothermic peaks in the differential thermal analysis curve can be assigned to the group of weaker bonded or free OH (Zn\(^{2+}\) -OH\(_2\) -OH\(_2\)), giving rise to higher stretching frequencies (3292 - 3531 cm\(^{-1}\)). The bonds in the group of weaker bonded OH are stronger for the cations Mn\(^{2+}\) and Ni\(^{2+}\), more electronegative than zinc cations.

Table 4 also shows some alterations after heat treatment in the \(\nu\)PO\(_4\)\(^{3-}\) vibration region in the range between 1200 cm\(^{-1}\) and 900 cm\(^{-1}\) in relation to the data in Table 3. It is thus possible to identify the phosphate coating of sample E-F1, heat treated at 413 K, by observing the absence of both doublets which became single peaks. For the samples E-F3 and E-F5, after heat treating at 413 K and at 393 K, the peaks at 1068 cm\(^{-1}\)/1001 cm\(^{-1}\) and 994 cm\(^{-1}\) disappeared.

Table 4: Band positions of the infrared spectra for the phosphate coatings applied on the electrogalvanized steel after heat treatment.

| Sample | Position of Bands (cm\(^{-1}\)) |
|--------|---------------------------------|
|        | \(\nu\) (OH) | \(\nu\) (H\(_2\)O) | \(\delta\) (H\(_2\)O) | \(\nu\) (PO\(_4\)^{3-}\) | \(\delta\) (PO\(_4\)^{3-}\) |
| E-F1   | 3314             | 1627              | 1075  | 619 |
| (413 K)|                  |                   | 1005  | 459 |
|        |                   |                   | 941   |     |
| E-F2   | 3274             | 1627              | 1105/1066 | 631 |
| (393 K)|                  |                   | 1004  | 938 |
|        |                   |                   | 938   |     |
| E-F3   | 3210             | 1624              | 1106  | 639 |
| (413 K)|                  |                   | 1018  | 951 |
| E-F4   | 3527             | 3262              | 1101/1066 | 629 |
| (393 K)|                  |                   | 994/1014 | 576 |
|        |                   |                   | 929   |     |
| E-F5   | 3392             | 1636              | 1118/1076 | 617 |
| (453 K)|                  |                   | 1021  | 934 |

4. Conclusions

The partial dehydration of the zinc phosphate coatings and the low-nickel zinc phosphate coatings started at a lowest temperature (393 K).

The \(\nu\)OH vibration peak, around 3500 cm\(^{-1}\), disappears at 413 K for the manganese and nickel modified hopeite and the manganese-modified zinc phosphate, and at 453 K for the high-nickel modified zinc phosphate.

Alterations in the spectra of phosphate coatings on steel after heat treatment in the \(\nu\)PO\(_4\)^{3-} vibration region were identified.

It is possible to identify the man-
5. Acknowledgements

This work was supported by the Research Support Foundation of Minas Gerais, FAPEMIG, Henkel Surface Technologies Brasil Ltda, and Usiminas Industry.

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