Characterization of Zinc and Manganese Phosphate Layers Deposited on the Carbon Steel Surface

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Abstract. The phosphating process is usually used to improve metals corrosion resistance properties. In this article, the carbon steel surface was coated with a phosphate layer based on zinc or manganese. Three types of phosphating solutions with different substances and concentrations were used for this process. The deposited layers were structurally characterized by Fourier-transform infrared spectroscopy (FTIR) in order to highlight the main compounds specific to the phosphate layers. In the same time, by means of this analysis it is possible to confirm and evaluate the formation of coating layer and its degree of hydration.

1. Introduction
Phosphate conversion coating is one of the most important and widely used metal coating techniques. Phosphating is a special surface treatment of metals which, by spraying or immersion in a phosphate bath and phosphoric acid, produces the chemical transformation of the metal surface. This coating technique is commonly used for steel. The metal surface transformation consists of the creation by conversion of phosphate crystals or compounds that improve the material corrosion resistance, facilitating the subsequent painting process [1].

By immersing the parts in acidic solutions based on zinc, iron or manganese, a solid, difficult to dissolve phosphate layer is created, by a chemical reaction, with the base material [2].

Therefore, coating the steel with phosphate layers has some advantages, including high protection against corrosion, reducing friction and gliding or electrical insulation properties improving, also, subsequent coating by paints or oils can be considered [3].

The deposition of phosphates on the surface of the metal is used in the car construction industry, in cars, shipbuilding, aircraft, in the oil industry and the refrigeration industry. Due to their insulating properties, phosphate coatings can also be used in the electrical industry [4, 5].

The metal coatings by phosphates deposition are, mainly, used in the car construction industry, shipbuilding, aircraft industry, oil industry and refrigeration industry. Due to their insulating properties, phosphate coatings can additionally be used in the electrical industry [6, 7].

Depending on the environment and the process conditions, the phosphate layers are of two types: crystalline or amorphous. Generally, the crystalline layers are preferred which are deposited on a substrate of ferrous materials such as carbon steel, weak alloy steel and cast iron. The phosphate layers deposited on non-ferrous materials, as well as on stainless steels, have an amorphous structure, the deposition process and the parameters used are different in each case [8, 9].
The crystalline phosphating of metallic materials is obtained by spraying or immersing with an acidic solution that contains metallic phosphates of the bivalent metals zinc, iron and manganese. The layers deposited on the metal surface do not change the properties of the base metal, such as hardness, elasticity or magnetic properties [10-13]. This paper aims to analyze the zinc, zinc-iron and manganese phosphate layers deposited on the surface of carbon steel from a structural point of view using Fourier-transform infrared spectroscopy (FTIR).

2. Materials and methods
The base material used in this work is a carbon steel utilized in the manufacture of personal protective equipment components, work equipment parts etc. [7]. The main chemical elements composition, except iron, are carbon (0.45%), manganese (0.98%), silicon (0.22%), chromium (0.17%) and copper (0.15%).

Three phosphate layers of different compositions (1-zinc-based solution; 2-iron/zinc-based solution and 3-manganese-based solution) were obtained and structurally tested.

In order to obtain a homogeneous and uniform deposited layer on the carbon steel surface, the sample was prior prepared by two steps. These two stages with the role of cleaning the sample surface, consist of:
- the first stage, degreasing, has the role of removing from the steel surface any fat particles (oils or greases) prior used against atmospheric corrosion.
- the second stage, pickling, has the role of removing from the metal surface most of the iron oxides appeared due to the prior corrosion.

After each stage, the sample is rinsed in water, by immersion, in order to remove the chemical compounds that have appeared as a result of metal surface degreasing and pickling.

Following these two stages, the samples were phosphate conversion coated by immersion in three types of phosphating solutions, with different compositions. The technological parameters of the phosphating process, the temperature and the pH of the solution, as well as the samples maintaining time in the solution, have been strictly controlled. After phosphating, the samples were dried at room temperature.

All three types of phosphate layers deposited on the carbon steel surface were chemical structurally analyzed using a Bruker Hyperion 1000 FTIR spectrometer in a wavelength range of between 4000 cm\(^{-1}\) and 600 cm\(^{-1}\) at a spectral resolution of 4 cm\(^{-1}\) and 64 scans for each surface analyzed, the interferograms obtained being analyzed using the OPUS 65 Bruker software.

3. Results and discussion
Structural characterization by Fourier-transform infrared spectroscopy was performed in order to highlight the main compounds specific to phosphate layers [14]. Furthermore, by means of this analysis, it is possible to confirm the formation of the coating layer and its degree of hydration.

The FTIR spectrum of the sample coated with a zinc phosphate layer graphically represented by the number of the wave on the abscissa and the intensity of the infrared radiation in absorbance per ordinate is shown in Figure 1.

As can be seen in Figure 1, the vibration band between 1100 and 850 cm\(^{-1}\) has several peaks of significant intensity. Their positioning at 871, 976 and 1055 cm\(^{-1}\) can be attributed to the stretching asymmetric valence bonds of the reaction products between phosphate and hydroxide in the form of PO or POH groups of complex compounds of HOPO\(_3\)\(^3\), PO\(_4\)\(^3\) and H\(_2\)PO\(_4\) being specific to phosphate layers deposited by conversion [15].

The vibration band between 3100 cm\(^{-1}\) and 3600 cm\(^{-1}\) with a significant peak at 3278 cm\(^{-1}\) is attributed to the hydroxide groups. Their presence may be due to the valence vibration of the adsorbed water, but also to the hydroxide group stretching from the hopeite structure (specific to zinc phosphate) [16].
The FTIR spectrum of the sample coated with zinc phosphate and iron presents three vibration bands, as can be seen in Figure 2.

Due to the similarity between the chemical composition of these two zinc phosphating solutions, the FTIR spectra present a large common proportion. The vibration band between 710 cm\(^{-1}\) and 680 cm\(^{-1}\) shows a peak at the wave number 687 cm\(^{-1}\) that can be attributed to the asymmetric valence vibrations of the metaphosphate groups. The appearance of the peaks in the vibration band between 1700 cm\(^{-1}\) and 1500 cm\(^{-1}\) corresponds to the adsorbed water molecules, which highlights the hydration degree of the zinc-iron phosphate layer [17]. Also, the vibration band between 3600 cm\(^{-1}\) and
3100 cm\(^{-1}\) which corresponds to the valence vibrations of the hydroxide groups is present, but also a band between 1100 cm\(^{-1}\) and 850 cm\(^{-1}\) which is attributed to the vibrations of the phosphate ions [18].

The large width of the vibration band between 1100 and 850 cm\(^{-1}\) is due to the different phosphate groups in the structure, the high number of vibrations in this area appears due to the bonds between these groups [16]. The peak positioned at 1111 cm\(^{-1}\) can be attributed to the asymmetric valence vibrations of PO\(_4^{3-}\) from the phosphophyllite structure, and the peak positioned at 969 cm\(^{-1}\) can be caused by the stretching and deformation vibrations of the P-O groups [19].

In the case of the samples coated with a layer of manganese phosphate, the FTIR spectrum shows major changes (Figure 3).

![FTIR spectrum of manganese phosphate layer](image)

**Figure 3.** FTIR spectrum of manganese phosphate layer.

The peak positioned at 918 cm\(^{-1}\) in the vibration band between 1100 and 850 cm\(^{-1}\) confirms the formation of manganese phosphate by the presence of P-O and P-O-H groups in Mn\(_3\)H\(_2\) (PO\(_4\))\(_4\)·4H\(_2\)O [17]. Moreover, the peak positioned at 3386 cm\(^{-1}\) is attributed to the hydroxide groups of complex chemical compounds [16]. While the band between 1700 and 1500 cm\(^{-1}\) is attributed to the deformation vibrations of the H-O-H groups in the adsorbed water molecules [20-22].

4. **Conclusion**

The FTIR spectra of the phosphate layers deposited by conversion present multiple similar vibrations bands that correspond to the hydroxide groups, but also different positioned bands that highlight the particularities of the formed compounds. In both the zinc phosphate and manganese layers, the spectrum presents a vibration band between 1100 cm\(^{-1}\) and 850 cm\(^{-1}\), which is assigned to the P-O and P-O-H groups. On this vibration band, sample 1 shows a high-intensity peak positioned at 976 cm\(^{-1}\), which confirms the formation of the hopeite, but after the introduction of Fe in the phosphating solution the main compound resulted on the surface is phosphophyllite, resulting in a high porosity layer with low crystallinity.

5. **References**

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