



Surface preparation for phosphate coating

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Abstract

Phosphate coatings are used to reduce friction and wear on machine parts. A phosphate crystalline base is used as an intermediate layer to receive subsequent treatments such as corrosion preventive oils or painting. In all cases the performance of the coverage depends on the quality and uniformity of the phosphate coatings. The aim of this work is to analyze the influence of the carbon steel plate surface pretreatment on phosphate grain size on manganese phosphate coating. The plate surfaces were prepared with wet emery paper, alumina and glass shot. The surfaces were examined by optical microscopy, scanning electron microscopy, X-ray diffraction and microprobe analysis. The results indicate that the surface finishing is relevant. A better surface finish provides a larger number of nuclei for phosphate crystal growth leading to a lesser crystal size. This suggested that the defects produced from surface preparation - which are present even at high quality finishing - are preferential sites for crystal nucleation. Other observations of the phosphate coatings show that the surface stress relief influences the manganese phosphate crystal quality. Before the phosphate crystal nucleation a corrosion process takes place, which is accelerated by the stress relief leading to a reduced phosphate crystal size.

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INTRODUCTION

Phosphating is the most widely used pretreatment, since: i) it serves as an excellent paint base, ii) increases corrosion resistance of metal paint, iii) aids in cold forming steel and increases the lubricant power of the oils applied to the pieces subjected to friction and wear.

The phosphating baths use a zinc phosphate, manganese phosphate, or iron phosphate base. Among these, the zinc phosphate is the most utilized, mainly as a base for paints. The manganese phosphate, which in most cases is utilized as a base for lubricant oils, given the high thickness of the obtained coating, can, eventually, serve as an excellent paint base (to be also utilized as a base for paints), mostly as a piece is half painted and half oiled [1]. In this case the pieces surface bears a chemical or mechanical treatment in order to thin granulometry of the phosphate coating, which is more adequate for painting [2]. The Mn and Zn phosphates are crystalline and their grain size influences in an inverse way the resistance to corrosion, i.e. for a painted system the smaller the grain, the greater the corrosion resistance [3]. The most utilized chemical refiners are a Ti salt base, which increase the preferential sites for chemical attack, increasing the number of nuclei for crystal growth, thus diminishing the final crystal size [1].

According to Ghali and Potvin [3], the phosphating mechanisms can be divided in four steps: 1) electrochemical attack ; 2) amorphous precipitation; 3) crystallization and growth; 4) crystalline reorganization. The electrochemical attack modifies the pH near the surface and propitiates a precipitation of secondary and tertiary phosphates , in an amorphous state, in the material surface. This amorphous structure crystallizes, the crystals grow , redissolve themselves and reprecipitate, reorganizing the structure. The first step of the phosphating mechanism is a corrosion action, so, the most active the surface, the quicker occurs the reaction and, consequently, thinner the grain. This way, the surface preparation has a great influence in the process, as other researchers have also concluded [4].

EXPERIMENTAL METHODS

All test runs were conducted on low carbon steel specimens with 20 x 20 x 1 mm. Samples of low carbon steel have been cutted in squares of 20mm x 20mm x 1mm. The samples surfaces before the phosphating have been prepared in four ways: jacteated with glass micro-sphere, sandpapered with sandpaper #100, sandpaper #400 and polished with alumina 3 μ m. After the surface preparation, the samples have been desengordurated with acetone and phosphating with a commercial product of manganese base for 10, 30, 60, 300 seconds.

Scanning electron microscope (SEM) with EDS system were conducted as a structural analyses of the phosphate coatings was carried out on an X-ray diffractometer to determine residual tensile stress. To characterize the performance of manganese phosphate coatings adhesion resistance were examined. A cross hatch test is a simple method and allows judging of the adhesion of a paint film on the phosphated steel.

After the phosphating the coating microstructure have been analyzed in the Scanning electron microscope (SEM) coupled with EDS, JEOL JSM-U3 (50kV), in 25 kV stress. It has also been utilized a X-ray diffractometer PHILIPS, in order to constate residual stresses due to the to the jacting with micro-spheres.

RESULTS AND DISCUSSION

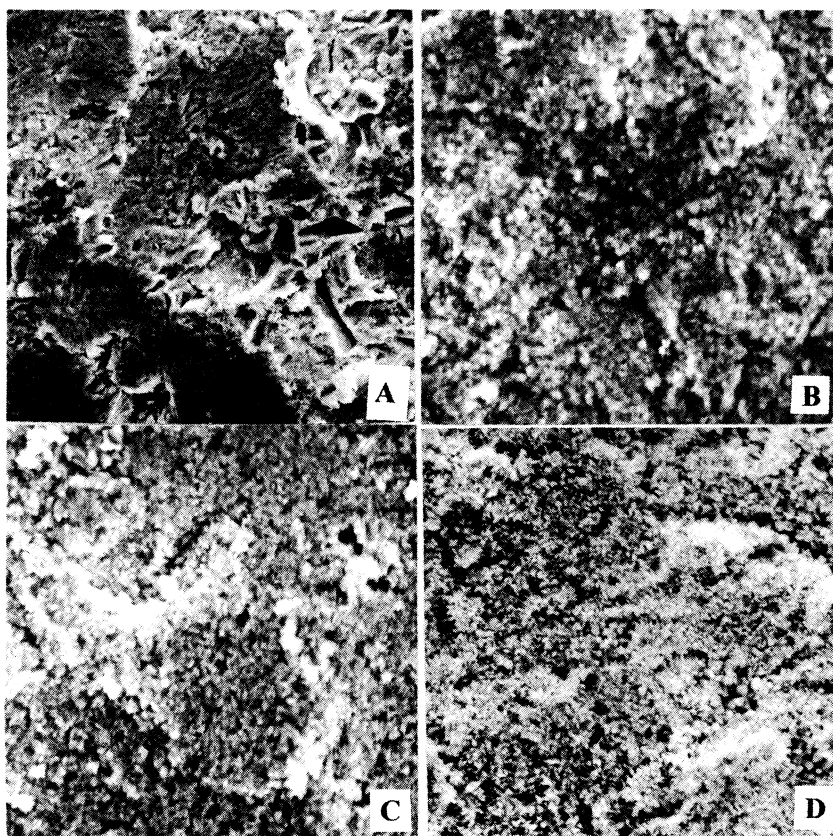
An X-ray diffraction pattern was first obtained for a plate steel test specimen as received and the results were compared for the specimens subjected to phosphate condition. Well defined diffraction lines corresponding to hurealite.

The appearance of the surface topography strongly depends upon the specimens preparation. As we can see on Figure 1 after 30 sec the surface is completely it can be observed that from the 30 sec phosphating the surface is already completely covered, though the crystalline structure is only perceived after 60s. Probably, the amorphous precipitation is completed around 30s, when there is a significative increase in the P and Mn contents. It has been observed at

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there is a significative increase in the P and Mn contents. It has been observed at bare eye, that the samples with time superior to 30s present surfaces with a black color, while for inferior times the observed color has been metallic gray, characteristic of the jacted steel with glass micro-spheres, which has been the decoating treatment utilized in the phosphating process.

Figure 1. Surface of carbon steel plate after glass shotted and phosphated during:
A) 10 s; B) 30s; C) 60 s; D) 300 s.



In the figure 2 it can be observed that the Fe perceptual diminishes with the increasing of the phosphating time, given the physical barrier imposed by the coating at measure it increases in thickness. The P and Mn contents increase in a sigmoidal shape with the increasing of time; at the end of the process the perceptual of Mn has a more accentuated increase. This increase can be associated to a substitution of the Fe by Mn in the hurealite (predominant phosphate in the coating obtained by phosphating at manganese base) [5].

In the Figure 3 we can notice , in sequence, an increase in the phosphate crystals size, they being very smaller in the jacted samples.

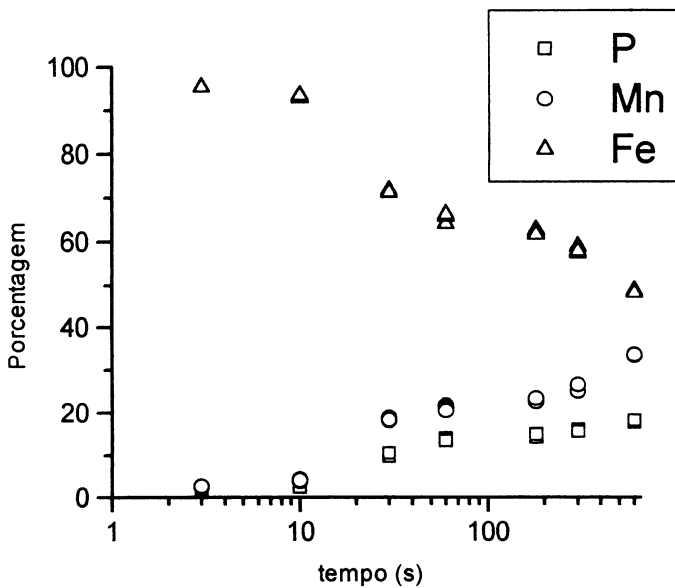
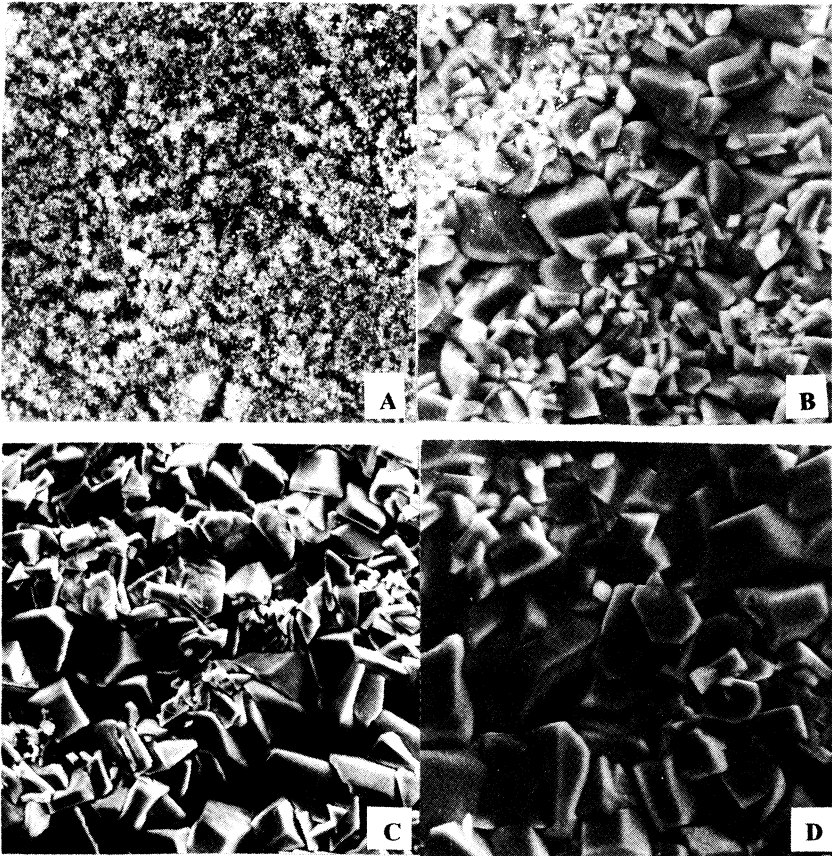


Figure 2 Graphical representation of the athomical perceptual of P, Mn and Fe for different phosphating times.

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Figure 3. Scanning electron micrographs show the effect of surface preparation on manganese phosphate coating on low carbon steel. Phosphate coating topography at manganese base. (A) lacted with glass micro-spheres; (B) prepared with wet emery paper number 100. (C) prepared with wet emery paper number 400; (D) polished with alumina $3\mu\text{m}$.



The first phosphating step is characterized by a dissolution of the metal base [3]. So, the more activated is the surface, the quicker is the phosphating process and smaller the grains. Smaller grains proportionate a smaller porosity and ,consequently, more resistance to corrosion.

A surface can be activated through refiners , as titanium salts, which form nucleation sites of corrosion, or through mechanical processes as the sandpiperling or jacting. This modify the surface rugosity, facilitating the atoms output. In the case of jacting, besides the increasing of the rugosity there are residual stresses, introduced during the preparation of the surface, which collaborate in the activation of the surface, promoting greater speed in the process.

The coating in sandpipered surfaces have heterogeneous grains, indicating that the process has a different kinetics for the various areas of the sample surface.

The coatings in polished surfaces, although do not be of industrial interest , serve as reference , as the polishing gives to the surface a greater resistance to corrosion in relation to that not polished and, in this case, it can be seen in the Figure 3D that the crystals are the greater, which is completely in accordance with the mechanisms proposed by GHALI and POTVIN [3].

CONCLUSIONS

- The P and Mn contents increase with the phosphating time.
- The surface preparation of samples with the jacting of glass micro-spheres activates the sample surface, not only by the increasing of rugosity, but also by the imposed residual stresses.
- The sandpiperling causes an heterogeneous phosphate coating.
- The preparation by mechanical processes, of the surface to be phosphated , is a factor which influences in the nucleation kinetics of the crystals.



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