

Blue and Green Phosphate Coatings Formed on Steel without Heating

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INTRODUCTION & AIM

The application of phosphate coatings is one of the simplest, most economical and reliable ways to protect parts, equipment and structures made of carbon and low-alloy steels and cast iron from corrosion.

Phosphate coatings protect the metal surface mechanically. They isolate the protected metal from the environment.

Fine-crystalline phosphate films, characterized by good anticorrosive properties, are obtained from solutions based on the Mazev Salt containing $Mn(H_2PO_4)_2 \cdot 2H_2O$ (proportion of phosphoric acid, in terms of P_2O_5 46–52% ; mass fraction of manganese not less than 14%). In such solutions, good-quality coatings are deposited on products made of structural steel and cast iron. To speed up the deposition of coatings, additives of accelerators, such as zinc nitrate, are introduced into the phosphating solutions. The use of additives also makes it possible to phosphatize the metal surface at room temperature.

Phosphates, which are part of phosphate films, have dielectric properties, therefore, the film is characterized by an electrical insulating ability.

Phosphate coatings undergo significant changes when the temperature changes. When they are heated above room temperature, a gradual weight loss occurs. The change in the appearance, color and morphology of phosphate coatings remains virtually unchanged up to 200 °C.

In the processes of metal phosphating, the composition of the solution, the mode and method of phosphating determine not only such properties of phosphate coatings as corrosion resistance, wear resistance, color, the nature of the crystal structure, but also their molecular nature.

In recent years, the requirements for the quality of phosphate coatings and their application technologies, including economic and environmental aspects, have significantly increased. Priority areas for improving phosphating processes are improving the protective and other functional properties of coatings, reducing the concentration of solutions, temperature and processing time, simplifying adjustments, unifying phosphating compositions, and reducing the environmental hazard of processes.

The conducted studies show that the modified coatings obtained by the cold method are not inferior in physical and mechanical properties to traditional phosphate coatings.

METHOD

Colored phosphate films are obtained from a phosphating solution of the composition [g/L]: Mazev Salt (containing $Mn(H_2PO_4)_2 \cdot 2H_2O$ (proportion of phosphoric acid, in terms of P_2O_5 46–52%; mass fraction of manganese not less than 14%) 35–45, $Zn(NO_3)_2$ 50–65, $NaNO_2$ 3–4, glycerin 1–2, trilon B 6–8, the preparation OS-20 5–10, by suspending in it the powders of procyon olive green and methylene blue dyes in an amount of 8 g/L for the deposition of green and blue films, respectively.

Phosphate coatings were deposited on the surface of samples made of St3 steel with dimensions of 100 × 50 × 3 mm. Steel samples were cleaned with sandpaper before deposition of the phosphate coating, then degreased in an alkaline hot solution, and then treated with an alcohol solution. The coating was formed on the surface of a steel sample immersed in a phosphating solution for 15 minutes at a temperature of 20 °C. After extraction from the solution, the sample was washed with running water and dried in air.

To determine the application areas of colored phosphate coatings, a few of their physical and mechanical properties are investigated.

The heat resistance of the phosphate films was tested at temperatures of 100, 200 and 300 °C by placing the samples in a muffle furnace for 2 minutes. After extraction of the samples and they cool down, the protective ability of phosphate coatings was tested by the drip method. A solution containing $CuSO_4 \cdot 5H_2O$ – 80 g/L, NaCl – 33 g/L, HCl (0.1 N) – 13 ml/L was applied to the surface of the sample, and the time of changing the color of the surface from blue to red was monitored.

The determination of coating thickness was carried out by measuring the thickness on microphotographs of the cross-section of the phosphated plate enclosed in the section, considering the multiplicity of magnification during microphotography.

The wear resistance of phosphate coatings was carried out on the installation for determining the coefficient of friction. Diagram of the friction disk on the disk. The rotating disc with a diameter of 0.04 m is made of St45 steel, the non-rotating disc is a sample with the test coating.

The breakdown voltage test of the electrical insulation coating is carried out on the electric spark flaw detector Corona 2M (Constanta-MSK, Moscow, Russia). The principle of its operation is to close the electrical circuit created by connecting the electrodes to the object under study and generating current by a high-voltage transformer. The signal received when a defect is detected is recorded by the device, which it notifies with the help of light and sound alarms. The device is equipped with a display for digital indication of the voltage level.

RESULTS & DISCUSSION

Figure 1 shows photos of modified phosphate coatings obtained by cold method on steel. Colored phosphate coatings turned out to be uneven, some areas of the steel surface remained uncovered. The green phosphate coating is coarse-grained and has a significant roughness. The blue phosphate coating turned out to be finely crystalline, but its appearance also requires improvement.

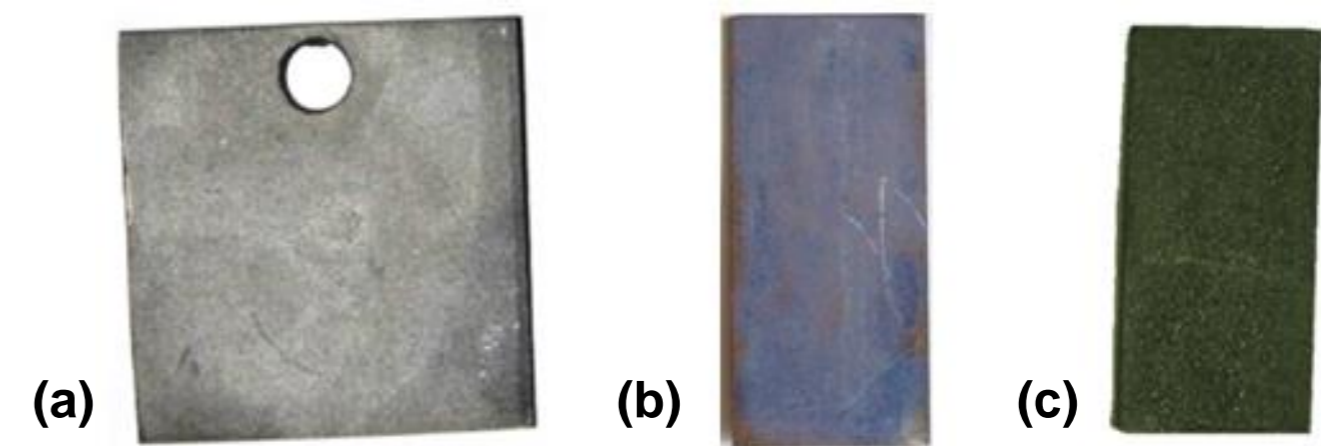


Figure 1. Images of phosphate coatings obtained at room temperature: (a) uncolored; (b) blue; (c) green.

The processes of cold chemical phosphating of metals proceed with self-inhibition due to the termination of access of the phosphating solution to the metal surface. Therefore, the thickness of the resulting phosphate coatings after reaching a certain limit does not significantly increase in the future. It is possible to judge the thickness of the coatings by the cross-section sections: the thickness of the modified phosphate films is 3–4 microns.

It is known that phosphate coatings can withstand short-term heating up to 400–450 °C. The results of the study of the heat resistance of phosphate coatings show (Table 1) that with increasing temperature, the protective ability of the coatings decreases, and when heated to 300 °C, the films lose their protective properties. In general, colored phosphate coatings obtained in solutions with dyes have less protective properties, which is due to their uneven distribution on the surface of steel, as can be seen in Figure 1.

Table 1. Results of tests of the protective properties of phosphate coatings by the drip method after heating.

Type of phosphate coating	Control time immediately after phosphating, sec	Control time after heating, sec		
		100 °C	200 °C	300 °C
Uncolored	460	135	75	3
Green	430	125	79	2
Blue	435	122	72	2

The coefficient of friction of the green phosphate coating has an uneven distribution over the thickness of the coating, its values are in the range of 0.05–0.2. This difference in the values of the coefficient of friction is explained by the fact that the surface of the product has a softer phosphate coating and a higher coefficient of friction, and the upper layers of the film are harder, and their coefficient of friction is lower. The blue phosphate coating turned out to be the most uniform in thickness of the studied ones. The friction during the tests was stable, the value of the coefficient of friction is 0.13. The modified phosphate coating is not uniform in thickness, and the friction during the tests was non-stationary. The values of the coefficient of friction are in the range of 0.1–0.15. Due to the low values of the coefficients of friction and heterogeneity in thickness, phosphate films obtained from cold phosphating solutions cannot be recommended as wear-resistant coatings, but they can be used to protect structural products, as well as to cover the elements of structures laid by drawing.

The modified phosphate films have sufficiently high electrical insulation properties (Table 2) due to their fine-crystalline structure, low porosity and uniform distribution on the metal surface. However, compared to the coatings obtained by hot phosphating, for which the average breakdown voltage is 250 V, the results are not high. The lower value of the breakdown stress in phosphate coatings obtained on steel by the cold method is because they are much thinner than coatings obtained from phosphating solutions when heated.

Table 2. Results of tests of the protective properties of phosphate coatings by the drip method after heating.

Type of phosphate coating	Breakdown voltage, V
Uncolored	200
Green	184
Blue	190

CONCLUSION

Modifying the compositions of cold phosphating solutions to obtain colored phosphate coatings on steel makes it possible to obtain phosphate coatings that have a small thickness, but good protective properties, and improve the performance characteristics of the protected products. Phosphate coatings can withstand short-term heating up to 100 °C, at a higher temperature, the protective ability of the coating decreases. The adhesion strength of the phosphate film to steel is very high. The wear resistance of the phosphate film is low. The electrical insulating properties of phosphate coatings meet the requirements, they do not change when the temperature rises due to overheating of electrical equipment up to 100 °C, the coatings are firmly bonded to the metal and protect it from corrosion.