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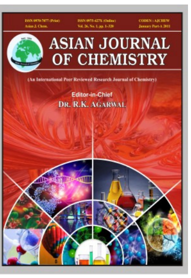

Preparation and Evaluation of Phosphating Solution for Room Temperature Applications

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The preparation of Zn-Mn-Ni phosphating solution (for room temperature applications) which uses nitric acid- sodium nitrate-sodium fluoride as the accelerant was described in this article. The film weight and corrosion resistance properties were investigated. The influences of fluorine, nickel and the manganese on the phosphating process were investigated and the corrosion resistances of the phosphating film were evaluated. The new system overcomes some disadvantages of phosphating at medium or high temperature such as high energy consumption, high cost and low efficiency. Using the proposed solution and process, the phosphation is stable in film formation. The resultant film is uniform in thickness, little sediment and excellent corrosion resistance.

Keywords: Room temperature, Zinc phosphating, Zn-Mn-Ni ternary system.

INTRODUCTION

Phosphating film is often used as the bottom layer in order to extend the life of the coating[1]. Phosphating at room temperature is the developing orientation of current phosphating technology. It is the most active, the fastest in development and the most important technology in the related area. Phosphating is a chemical process involving the formation of phosphate layer on metal surface. Based on national standards, the steel surface has to go through oil removal, rust removal and phosphating passivation, powder coating and electroplating to improve its corrosion resistance and the coating adhesion[2-7]. By adding strong oxidant, complexing reagents and surfactants in the experiment, we can improve the uniformity of the film, get desired thickness of the film, and make the phosphating solution relatively stable in use, improve the durability and reduce the phosphating sediment. The new phosphating solution is simple for operation. It is applicable to the phosphation of various parts with special requirements such as those of cars, refrigerators, air conditioners and cabinets.

EXPERIMENTAL

Phosphating process: Workpiece oil removal (PA-66, 65 °C, till indetectable) → washing (room temperature), 1 min) → rust removal (25 % sulfuric acid + 5 % thiourea, 55 °C, till none) → washing (room temperature, 1 min) → surface treating (surface treating of colloid titanium phosphate, 0.1g/L, room temperature, 30s) → phosphating → washing (room temperature, 1 min) → drying Phosphating formula and phosphating conditions: Formula of phosphating solution is as follows (g/L): Phosphoric acid (85 %): 16-20; nitric acid: 3-4; zinc oxide: 5-7; nickel salt: 0.2-0.5; manganese salt: 0.2-0.5; sodium fluoride: 0.4; sodium tripolyphosphate: 0.02; potassium sodium tartrate: 0.5; surfactant OP: 0.005-0.01; sodium nitrite: 0.2; sodium dodecyl benzene sulfonate: 0.005-0.01; deionized water: allowance. The phosphating condition are total acid: 21-28; free acid: 0.8-1.0; T: 30-50 °C.

Corrosion resistance: The corrosion potential of the phosphating film was determined. Generally better potential comes to the better corrosion resistance.

Film weight: According to GB/T9792, the film weight of test piece before and after the phosphating was determined on an analytical balance.

RESULTS AND DISCUSSION

Effects of fluorine ions on phosphating: This formula uses nitric acid-sodium nitrate-sodium fluoride as the oxidation promoters. Figs. 1 and 2 show the effects of fluorine ions on the film weight and the film potential when other components kept constant.

In the phosphating, a certain amount of F- is often introduced in the form of NaF or KF. In the phosphating reaction, when hydrogen ion concentration reduces, the reaction goes toward the formation of phosphating film, and the rate accelerates.

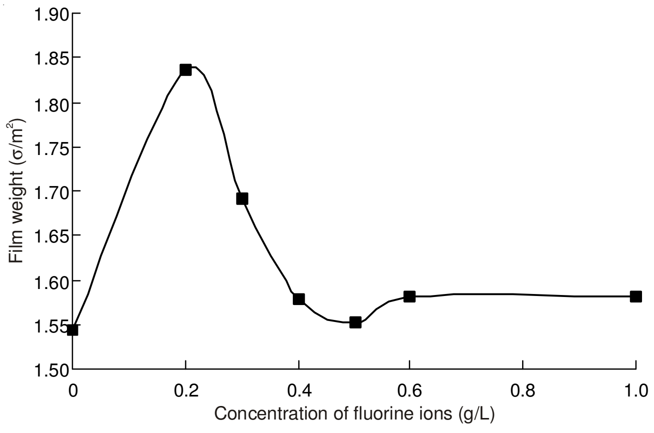

Fig. 1. Effects of fluorine ion content on film weight

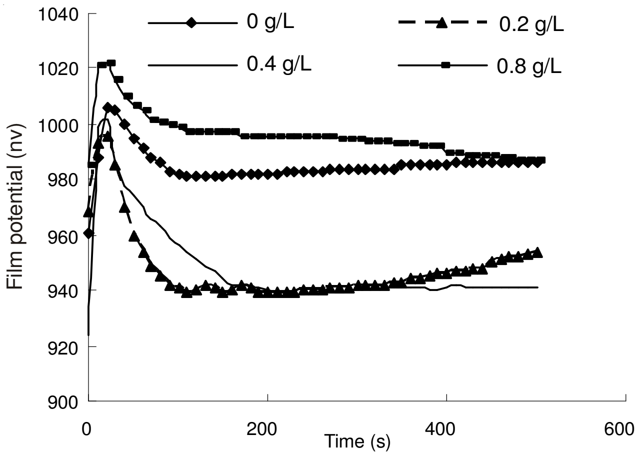

Fig. 2. Effects of fluorine ion on film potential

Fluoride has two main effects on phosphating: (1) as a pH buffering agent, stabilize the pH of the solution; (2) F^- is an effective accelerant to the phosphating at low temperature. In low temperature phosphating, the corrosion of metal is slow which will hinder the whole phosphating process. Addition of F^- can promote the corrosion of metal, and leads to the formation of an active zone on substrate surface which is beneficial to the nucleation of phosphate crystal, thus accelerating the phosphating process. Fig. 2 showed that addition of NaF or KF can increase the corrosion potential of iron in the phosphating solution, which indicates that the corrosion resistance of the resultant film can be effectively improved because of the thinner grain and the denser structure.

Effects of nickel ions and manganese ions on phosphating solution: Nickel and manganese are both divalent metals whose potentials are higher than that of zinc. They can participate in the film process and partly replace the iron ions in the phosphating film to form new active crystal center. Figs. 3 and 4 show the effect of nickel and manganese ions on the film weight and alkali corrosion resistance of the phosphating film.

It can be found that adding 0-2 g/L Ni^{2+} and Mn^{2+} will reduce the film weight, while more than 3 g/L the film weight will slightly increase.

From Figs. 5 and 6, it is clear that the addition of nickel and manganese can evidently reduce the weight loss of the phosphating film by alkali corrosion. When the adding amount

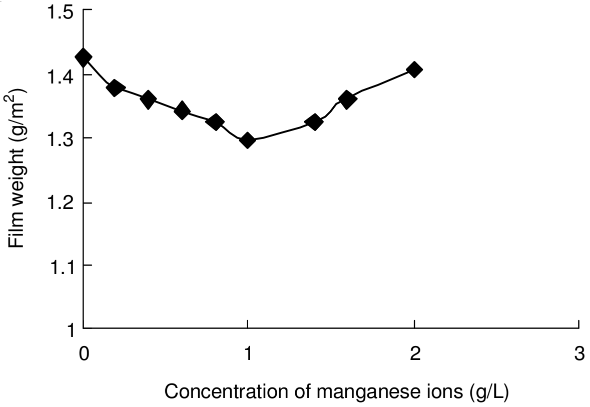

Fig. 3. Effect of manganese ions on film weight

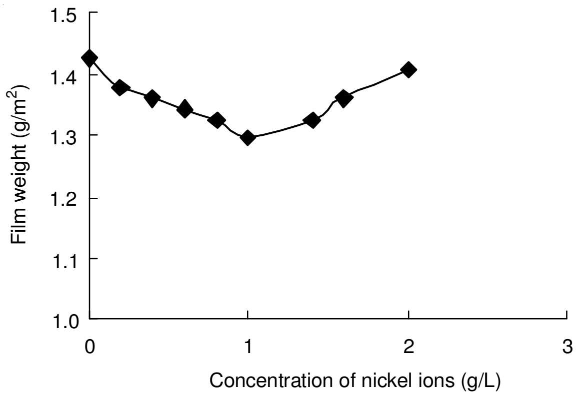

Fig. 4. Effect of nickel ions on film weight

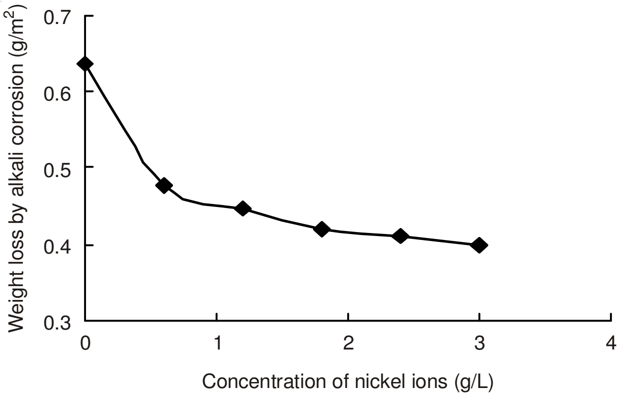

Fig. 5. Effects of nickel ions on alkali corrosion resistance of the film

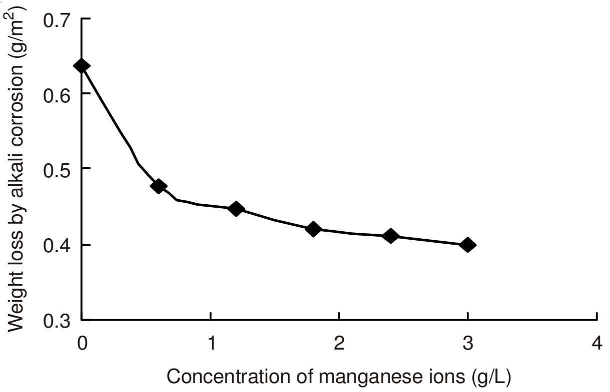

Fig. 6. Effects of manganese ions on alkali corrosion resistance of the film

is less than 0.2 g/L, the nickel and manganese in the phosphating film is not sufficient and the alkali resistance is relatively poor. However, 0.6 g/L Ni^{2+} and Mn^{2+} can evidently increase the alkali corrosion resistance. When adding the same amount of Mn^{2+} and Ni^{2+}, Mn^{2+} shows better film's alkali corrosion resistance of Ni^{2+}.

In this formula, the phosphating solution contains not only Mn^{2+} but also Ni^{2+}. In order to exploit their synergistic effect, the amount of Ni can be relatively reduced when adopting the Zn-Mn-Ni ternary system. Figs. 7 and 8 below are the characterizations of Mn-Ni synergistic effect on the film weight and the alkali corrosion resistance of the phosphating film when using different ratios of Ni^{2+} and Mn^{2+}.

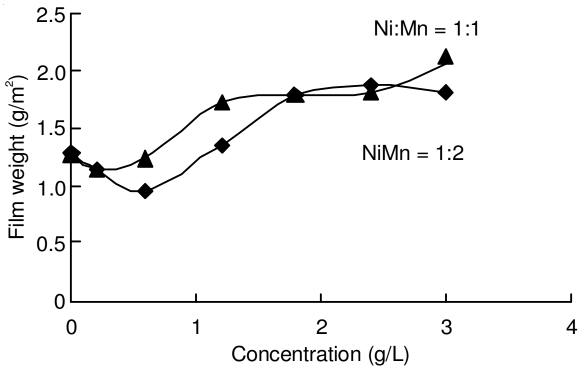

Fig. 7. Effects of Ni, Mn on film weight

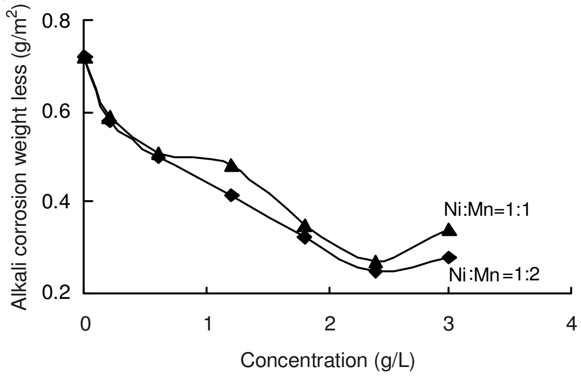

Fig. 8. Effects of Ni, Mn on alkali corrosion resistance

It can be seen from Figs. 7 and 8 that the phosphating solution with Zn-Mn-Ni ternary system can increase the film weight, and this trend is more obvious when the Ni: Mn ratio is 1:1 than that of 1:2. In addition, Ni and Mn will largely strengthen the alkali corrosion resistance of the phosphating film. Furthermore, we found that it will not do any good if the volume of Ni is too little, while it will not have any adverse effects if the volume is large.

Effects of phosphating time: Phosphating time is an important influencing factor. Reducing phosphating time can improve the working efficiency. However, phosphating film can only have a significant protective effect when the film completely covers the entire metal surface. Fig. 9 shows the relationship between the phosphating time and the film weight.

It is observed that the film forms mainly within 60 s. After 60 s, the film weight increases a little. After 120 s, the phosphating film weight remains stable, which indicates that the film has completely covered the surface and a complete phosphating film has formed.

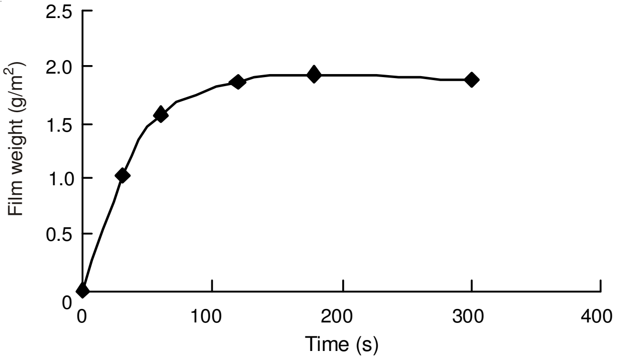

Fig. 9. Relationship between phosphating time and film weight

Effects of temperature: Effects of temperature on the performance of phosphating solution are shown in Table-1.

TABLE-1
EFFECTS OF TEMPERATURE ON THE PHOSPHATING SOLUTION AND THE RESULTANT FILM

Temperature (°C)	Appearance of phosphating solution	Film forming time(min)	Appearance of phosphating film
10	Transparent light green	Approximately 3	Grey phosphating film, partly discontinuous uniform
20	Transparent light green	Approximately 2.5	Grey phosphating film, poor uniformity
30	Transparent light green	Approximately 1.5	Grey uniform film
40	Transparent light green	Approximately 1.5	Grey uniform film
50	Transparent light green	Approximately 1	Grey uniform film
60	Transparent light green	Approximately 1	Grey uniform film, a few crystals on the surface
70	Transparent light green crystals in the bottom	Never	—

Appropriate increase in the temperature can activate low energy points on the workpiece to form "active center", which may increase the amount of crystals and accelerate the crystallization rate. However, if the temperature is too high, the reaction rate will be too fast, the film layer will be thick and the gap is relatively large, which will form phosphating film with slag, reducing the corrosion resistance and leading to poor stability of the solution. As shown in Table-1, when the temperature is between 30 and 50 °C, the phosphating rate and the quality of the film layer can be guaranteed. In addition, it can reduce the sediment and is beneficial to keep the solution stable.

Effects of acidity: The total acidity, free acidity and their ratio in the phosphating solution are the important factors which affect the film quality.

Fig. 10 shows the film potential-time curves under different free acid (FA). It is clear that the surface potential of the phosphating film is the highest when the free acidity value is

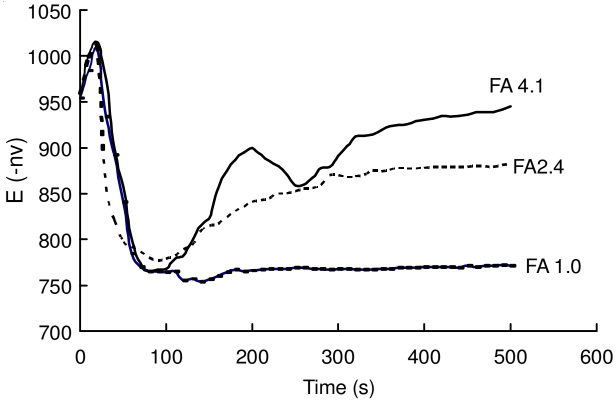

Fig. 10. Film potential-time curves under different free acidities

1.0, thus the corrosion resistance is the strongest at that point. In applications we should always pay attention to the change of free acidity and make timely adjustments.

Conclusion

This process belongs to ternary zinc phosphating at normal temperature. The adding of Mn^{2+} and Ni^{2+} is helpful for film formation and can largely improve the corrosion resistance of the phosphating film. Mn^{2+} is better in increasing the alkaline corrosion resistance of the film than that Ni^{2+}. The operational temperature of phosphating process is between 30 °C and 50 °C.

Phosphating by the proposed method can form a complete film in 2 min. The free acidity should be effectively controlled in using to improve the quality of the phosphating film.

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