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Preparation of Phosphate Coating Solution to Increase the Corrosion Resistance of Carbon Steel in Ambient Conditions

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Abstract

In this work, different zinc phosphating solutions were prepared using sodium phosphate (Na_3PO_4), sodium nitrate ($NaNO_3$), and nickel carbonate ($NiCO_3$) as accelerators. $NaNO_3$ concentration was ranged from 20 to 80 g/L. While the $NiCO_3$ concentration ranged from 1 to 15 g/L. To identify the interactions between the $NaNO_3$and $NiCO_3$, mixed accelerators were also investigated. Corrosion inspection of the metal surface was tested using potentiostatic experiments. Portable camera microscope was used to capture the surface images of coated samples. The experimental investigations revealed that the immersion time of 10 min significantly enhanced the corrosion tendency of all accelerators. It was noticed that the corrosion resistance was enhanced with more concentration of $NaNO_3$in the phosphate solution and reached their maximum protection at 80 g/L. While 1 g/L of $NiCO_3$ in solution (which represents the lower value), exhibited higher protection against corrosion. Mixed accelerators resulted in smaller grain size with lower corrosion current (1.83 mA) at 80 g/L and 5 g/L of $NaNO_3$ and $NiCO_3$, respectively. It was also found that chromic acid concentration significantly affected the corrosion resistance.

1. Introduction

Different methods have been used to mitigate corrosion such as inhibitors, anodic/cathodic protection, and coatings. The surface treatment, which includes polymeric coating, electroplating, and electroless plating have been widely employed [1]. These processes act to increase the paint adhesion, improve adhesion of the organic topcoat, and promote electrical insulation.

Among these techniques, the phosphating process is a well-known surface treatment that is used to protect metal surface from corrosion [2]. Basically, this method depends on electrochemical reactions in which the dissolution of the metal occurs at the anode sites coupled with the discharge of hydrogen. On the other hand, the hydrolysis and precipitation of insoluble phosphates occurs at the cathode sites.

In general, phosphating solutions combine from diluted phosphoric acid and primary phosphates of the metal ions [3]. Acceleration of the phosphating reactions is important to increase the process efficiency using chemical or mechanical methods [4]. Chemical accelerators found wide acceptance in many industrial processes.

For instance, at low temperature of phosphating bath, the implementation of nitrites as accelerator is the most common one [5]. The Ni^{2+} ions were found to accelerate the surface reactions during the phosphating process [6]. It was reported that the chemical composition of phosphate solution affected on alkaline stability [7]. For instance, the present of Ni and Mn ions was found to increase the alkaline stability of phosphate layers [8]. N. Satoh reported in his work that Ni^{2+} ions were able to refine the grain size of the zinc phosphate coating and enhance the protection against corrosion [9]. In another report, it was found that the addition of Ni^{2+} ions into the phosphating bath helps in improving the corrosion resistance and increase thickness of the coated layer [10]. The main obstacle in the implementation of phosphate coatings in a corrosive environment is the presence of open pores and pinholes [11]. The pore size and its population density on the phosphating coating were influenced the corrosion resistance. In which, the pores are considered a weak point on the phosphating layer and consequently allow the aggressive medium to start attacking the substrate surface.

The aim of this work is to investigate the protective abilities of zinc phosphate coating in sodium chloride solution. Different phosphate coating solutions will be prepared using sodium nitrate, tri-sodium phosphate, and nickel carbonate activators. Other parameters will be also investigated such as immersing time and washing solution composition.

2. Materials and Method

2.1. Materials

Zinc oxide, phosphoric acid, nitric acid, sodium nitrate, tri-sodium phosphate, hydrochloric acid, sodium hydroxide, chromic acid, and nickel carbonate are analytical grade and were purchased from local market.

2.2. Sample Preparation

Low carbon steel samples (2 cm × 2 cm) were adapted by grinding and then degreasing by immersion in caustic soda solution (50 g/L) and then flushed with distilled water to remove any traces of oil. After that, the sample was immersed in diluted hydrochloric acid (1:3 vol% of acid: water) for 2 min to remove the oxide layer from the surface and then flushed with distilled water to remove acid traces from the sample. These processes were adapted directly before phosphate coating for all coated samples.

2.3. Phosphate Bath

Stock solutions of the phosphate bath were selected depending on previous works [2, 12] and pre experiments as shown in Table (1). To prepare phosphate bath solution, 10 ml was taken from each stock solution and diluted to 250 ml by adding distilled water. The parameters studied in this work and their ranges were tabulated in Table (2).

Table (1). Composition of phosphate bath.

Bath composition	A	B	C
ZnO(g/L)	160	160	160
H_3PO_4(ml)	380	380	380
HNO_3(ml)	142	142	142
Na_3PO_4 (g/L)	3	---	---
$NaNO_3$ (g/L)	---	60	---
$NiCO_3$(g/L)	---	---	10

Table (2). Studied parameters.

Parameter	**Range**	**Unit**
Immersion time	5 - 30	min
$NaNO_3$	20 - 80	g/L
$NiCO_3$	1-15	g/L
$NaNO_3$ (g)	80	g/L
$NiCO_3$ (g)	1-5	g/L

2.5. Corrosion Measurement and Sample Characterization

After each coating experiment, the samples were washed with distilled water and dried in air. The corrosion behavior of phosphate samples was studied in 3.5 wt.% NaCl solution at ambient temperature (25 °C ±2). The electrochemical measurements were achieved using a potentiostat MLab 200) with a three-electrode system. The working electrode was carbon steel covered with the phosphate layer. While, the counter electrode was Pt with a saturated Ag/AgCl as a reference electrode. All potentials were reported versus a reference electrode (saturated Ag/AgCl). The open circuit potential (E_{corr}) of electrodes in the solution was monitored for 1 h. The average of three reading data of E_{corr} values were taken. Surface morphology of coated samples were monitored using portable microscope.

3. Results and Discussion

To investigate the performance of zinc phosphate coating, the parameters were taken included immersion time, accelerator concentration, and accelerator type. These parameters will be discussed as indicated below:

3.1. Immersion Time

Immersion time is an important parameter in industrial application of zinc phosphate coating. Immersion time set from 5 to 30 min as indicated in Table (3). As shown in this table, the corrosion current (I_{cor}) for A, B, and C solutions were varying with time. However, there were no significant changes in $I_{cor.}$ values for all solutions at immersion time greater than 10 min. Therefore, immersion time of 10 min will be set in the upcoming experiments. Referring to corrosion data in Table (3), the corrosion current of solution A was relatively higher among other accelerators. Therefore, the current study will focus on studying the effect of changing the concentration of sodium nitrate and nickel carbonate in the phosphating bath.

Table (3). Effect of immersion time on corrosion behavior.

	I_{cor} (mA/Cm^2)			
Time (min)	A	B	C	Blank
5	7	4.51	7.05	-
10	5.86	5.45	8.71	10.73
20	5.54	5.33	5.73	-
30	4.64	5.24	5.23	-

3.2. Sodium Nitrate Concentration (“B” solution)

Accelerator concentration is an important parameter that directly affected on coating properties of zinc phosphate coating. Sodium nitrate was widely used in phosphate coating and its concentration was studied in different investigations. Various concentrations were taken from 20 g/L to 80 g/L as shown in Table (4). The corrosion current was found to decrease with increase in concentration of sodium nitrate.

Tian et. al [13] were used a-zirconium phosphate (α-ZrP) as an accelerator in phosphating bath coating to improve corrosion resistance of carbon steel. The results demonstrated that the incorporation of α-ZrP was effectively improved corrosion resistance of phosphate coating. In which, lower corrosion rate was obtained at 0.8 g/L of α-ZrP in the phosphating solution. Interestingly, Fang and his group used eco-friendly hydroxylamine sulfate in the phosphating bath to reduce the pollution as well as to improve the corrosion resistance [14]. The addition of hydroxylamine sulfate was successfully decrease the deposition time as well as reduce the grain size of the deposited layer.

Table (4). Effect of Sodium Nitrate concentration (solution B).

$NaNO_3$ (g/l)	I_{cor} (mA/Cm^2)
20	5.94
40	2.63
60	5.45
80	1.06

3.3. Nickel Carbonate Concentration ("C" solution)

According to Nickel carbonate accelerator (C solution), the investigated concentrations ranged from 1 g/L to 15 g/L as tabulated in Table (5). The corrosion tendency was shown to increase with the concentration of nickel carbonate. The best concentration of $NiCO_3$ was 1 g/L in which the corrosion current was minimize at this point.

The role of present Ni^{+2} in zinc phosphate bath were investigated by Akhtar and coworkers [15]. They claimed that the increased in the corrosion resistance of Al is due to the presence of $NiAl_2O_4$, which resist corrosion than aluminum oxide. In another work, it was found that the addition of Ni^{+2} to the phosphating bath improved the corrosion resistance as well as the adhesion of coating layers due to formation of Ni deposits on the base of pores of zinc phosphate layer [6]. Thus, the addition of nickel carbonate was shown to enhance the phosphating process. However, the increase in nickel carbonate concentration resulted a raise in corrosion rate. More elaboration on lower concentration range will be planned as a future work.

Table (5). Effect of Nickel carbonate concentration on corrosion current.

$NiCO_3$ (g/L)	I_{cor} (mA/Cm^2)
1	3.5
3	3.6
5	4.3
10	8.71
15	8.19

3.4. Mixed Accelerator Effect

To identify the interaction and the effect between accelerators used in this work, mixed accelerators experiments were performed. The best concentration of sodium nitrate (80 g) with various concentrations of nickel carbonate was tested as seen in Table 6. It was found that the present of nickel carbonate with sodium nitrate has a negative effect on corrosion tendency (I_{cor}). To elaborate this finding, the coated surface was investigated using portable camera microscope as shown in Figure (1). It was observed from this figure that the holes on surface decreased with $NiCO_3$ concentration. Therefore, 80 g of $NaNO_3$ with 5 g of $NiCO_3$ is the best composition in which the corrosion current reached to 1.83 mA.

However, from the previous experiments, it was shown that the present of $NaNO_3$ at 80 g in the bath solution reduced the corrosion current to 1.06 mA. This will lead us to conclude that there is no significant use of $NiCO_3$ with $NaNO_3$ in phosphate bath solution.

Table (6). Mixed accelerators ($NaNO_3$ and $NiCO_3$).

#Formula	$NaNO_3$ (g)	$NiCO_3$ (g)	I_{cor} (mA/Cm^2)
#1	80	1	5.6
#2	80	3	3.57
#3	80	5	1.83

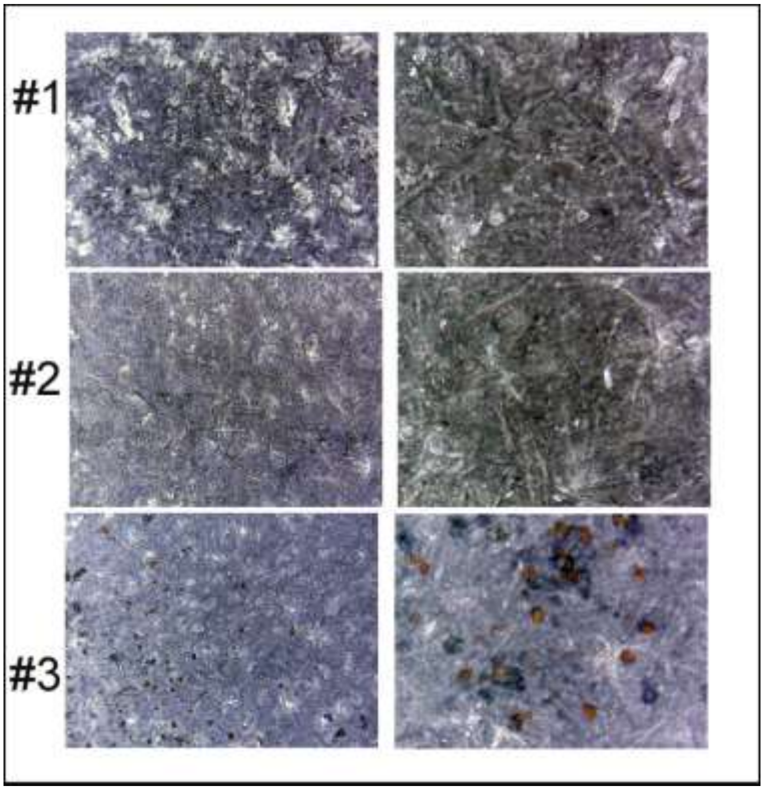

Figure (1). Surface images of mixed accelerators ($NaNO_3$ and $NiCO_3$).

3.5. Chromic Acid Concentration

In the final stage of phosphate coating, the sample needs to dip in chromic acid to detach the un-reacted molecules from metal surface and to seal the coating surface. This will help in producing a uniform coating layer. The best phosphate bath composition is the mixed of 80 g with 5 g of $NaNO_3$ and $NiCO_3$, respectively. Table (7**)** exhibited corrosion behavior of coated samples at different concentrations of chromic acid. As mentioned earlier, one of the functions of chromic acid is to seal the pores that present on phosphate layer. This will prevent the solution (in this case NaCl) molecules to pass through coating layer and subsequently attack the substrate surface. It is clearly found that the best concentration of chromic acid achieved at 0.1 % in which, the corrosion current was minimized at this value.

Table (7). Effect of chromic acid concentration on corrosion current.

CrO_3 (wt. %)	I_{cor} (mA/Cm^2)
0.05	1.99
0.1	1.26
0.2	2.97

4. Conclusions

It was found that there is no significant change in corrosion resistance when immersion time was more than 10 min. Increasing in sodium nitrate concentration has a positive effect on corrosion mitigation in 3.5 wt.% of NaCl solution and the best concentration was 80g/L. The nickel carbonate shows the best corrosion resistance at lower concentration (1 g/L). Mixed accelerators shows good corrosion resistance using 80 g of sodium nitrate with 5 g of nickel carbonate. A smaller grain structure was obtained at this concentration. The best chromic acid concentration was found to be 0.1 wt.% in which the corrosion current achieved lower value.

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