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# Surface Morphology and Anticorrosion Properties of Zinc Phosphate Coating Deposited with Various Concentrations of Zinc Oxide

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**الملخص**— في هذا البحث تمت دراسة تأثير تركيز أوكسيد الزنك في تطور البنية المجهرة ومقاومة التآكل لطبقة فوسفات الزنك المترسبة على سطح الفولاذ. تم ترسيب الطبقة على سطح الفولاذ من محاليل الفوسفات التي تحتوي على تراكيز مختلفة من أوكسيد الزنك (1.25 الى 10 جم/لتر). طبيعة سطح الطبقة وتركيبها تم الكشف عليها عن طريق جهاز الماسح الإلكترون الميكروسكوبي والتحليل الطيفي لتشتت الطاقة (SEM&EDS)، أما بالنسبة لخصائص مقاومة التآكل للطبقة فقد تم تقييمها عن طريق اختبار الغمر في محلول كلوريد الصوديوم (3.5%) واختبار رش الملح في نفس المحلول بتركيز 5%. اظهرت نتائج الدراسة أن زيادة تركيز اوكسيد الزنك في محلول الفوسفات تؤدى الى سرعة ترسيب الطبقة وزيادتها على سطح المعدن. اختبار الغمر اظهر أن مقاومة التآكل لطبقة فوسفات الزنك زادت مع زيادة اوكسيد الزنك، لكن اختبار الرش بالملح أظهر أن التآكل تحت الطلاء المعدني لمختلف طبقات الفوسفات زاد بزيادة اوكسيد الزنك في المحلول، وكانت أفضل مقاومة للتآكل تحت طبقة الطلاء عندما كانت نسبة اوكسيد الزنك في المحلول تتراوح ما بين 2.5 الى 3.5 جم/لتر. هذه النتائج تبين ان طبقة فوسفات الزنك مع نسبة قليلة من اوكسيد الزنك تكون جيدة وتعطى خصائص مقاومة للتآكل ممتازة عندم تستخدم كطبقة اولية قبل عمليات طلاء المعادن النهائية.

**الكلمات المفتاحية**—عملية الفوسفات؛ فوسفات الزنك؛ التآكل؛ حماية المعادن.

**Abstract**—In this investigation, the influence of zinc oxide concentration on the microstructural evolution and corrosion resistance of zinc phosphate coating formed on mild steel was studied. Phosphate layers were deposited from phosphating bath containing different concentrations of zinc oxide (1.25 ~ 10 g/L). The surface morphology and composition of phosphate coatings were investigated via scanning electron microscopy (SEM), and energy-dispersive spectroscopy (EDS). Corrosion behavior of the formed coatings was evaluated using immersion test in a 3.5% NaCl solution and salt spray test in 5% NaCl. The results showed that the increase in zinc oxide content facilitated the precipitation of phosphate coating and increased its surface coverage. Immersion test results revealed that the corrosion resistance of the phosphate coatings was markedly improved as the zinc oxide concentration increased. However, the salt spray test results showed that the underfilm corrosion of phosphated-painted steel was increased as the zinc oxide content increased to high levels. The best underfilm corrosion performance was observed for the coatings obtained with phosphating bath containing 2.5 and 3.5 g/L of zinc oxide. This behavior indicates that low zinc phosphate coating serves as a good pretreatment process for subsequent organic painting finishes.

**Keywords**— Phosphating; Zinc phosphate; Corrosion; Metal protection

## 1. Introduction

Zinc phosphate conversion coatings have been used widely in order to promote adhesion and corrosion resistance of painted metals [1-4]. They play a significant role in the automobile, process and appliance industries because of their excellent corrosion protection and adhesion [5, 6]. Conventional zinc phosphate coatings are formed on metal surfaces in solutions containing zinc ions, phosphate ions, and some accelerating ions such as chlorates, nitrate, and organic nitro compounds to promote the oxidation and dissolution of the metallic surface [6,7].

The phosphate layers consist mostly of hopeite and phosphophyllite phases when formed from zinc phosphating baths. Mechanism of the coating formation is shown in Fig. 1. Two main phases are usually formed on steel surface. Hopeite ($Zn_3(PO_4)_2.4H_2O$) is precipitated by chemical reactions between $Zn^{2+}$ and $PO_4^{3-}$ ions in the coating solution when the pH at metal-bath interface increased well into the basic range due to hydrogen reduction [8]. Phosphophyllite is deposited when iron ions incorporated in the coating bath besides above-mentioned ions [9]. These insoluble phosphate depositions are formed according to the following reactions [10,11]:

$$3Zn^{2+} + 2\,PO_4^{3-} + 4H_2O \rightarrow Zn_3\,(PO_4)_2\,.4H_2O \text{ (hopeite)} \quad (1)$$

$$2Zn^{2+} + Fe^{2+} + 2\,PO_4^{3-} + 4H_2O \rightarrow Zn_2\,Fe(PO_4)_2\,.4H_2O \text{ (phosphophyllite)} \quad (2)$$

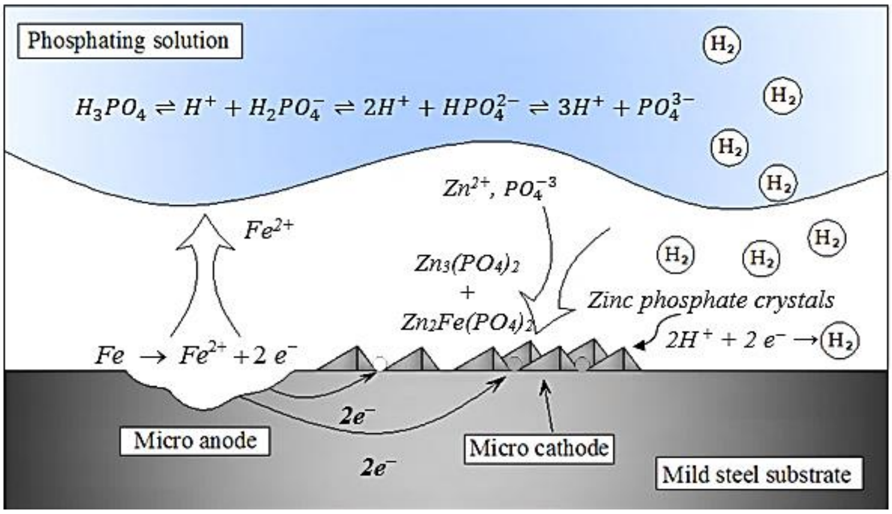


**Figure 1**. Diagrammatic representation of zinc phosphating reaction on steel surface

The performance of phosphate coating on steel depends on the fraction of the total surface area covered by the deposit and its composition [12, 13]. Many studies have revealed that phosphate layers with high content of hopeite phase are not desirable for subsequent organic coating finishes, especially electrochemical painting. Phosphophyllite phase is stronger and more stable in alkaline media than hopeite and can withstand the environment that is existing during the cathodic electrophoretic painting [14]. The quantitative ratio of these two insoluble phases in the formed coating is strongly controlled by the amount of zinc ions used in the phosphating solutions [15]. Based on Equations (1) and (2) which indicate the zinc cations are the main ingredient for coating forming species, the surface coverage, coating characteristics and the rate of coating deposition will be also influenced by the concentration of zinc ions in the phosphating solution [16].

Since $Zn^{2+}$ is an important ion in the formation of zinc phosphate coatings, hence the aim of this study was to investigate the effect of zinc oxide concentration on the formation, characteristics, and corrosion behavior of zinc phosphate coating formed on mild steel. The surface morphology and chemical composition of the coatings were analyzed using scanning electron microscopy (SEM), and energy-dispersive spectroscopy (EDS). The corrosion behavior of the phosphated samples was examined using immersion test in a 3.5% NaCl solution, whereas the underfilm corrosion was studied by evaluating the spreading of corrosion from the 'X'-scribe after 48 h of exposure in salt spray test.

## 2. Experimental

### 2.1. Sample preparation

Mild steel samples (15 × 10 × 2 mm) were used in this study; the chemical composition is given in Table 1. The substrates were mechanically polished using a series of emery papers up to 600 grits. Then the samples were subjected to ultrasonic cleaning in acetone and rinsed with deionized water. Thereafter, specimens were immediately immersed into the phosphating bath containing different amounts of zinc oxide for 5 min. The chemical composition and operating conditions for the phosphating bath are listed in Table 2; pH of the bath was adjusted by adding a 50% NaOH solution. Finally, the phosphated samples were rinsed with deionized water and dried with compressed air. The phosphate coating weight determination was calculated according to the following formula [17]:

$$W = \frac{W_1 - W_2}{A} \qquad (3)$$

where $W$ is the phosphate coating weight per unit area, $W_1$ is the specimen weight after phosphating, $W_2$ is the specimen weight after the coating was eliminated using a 5% chromium trioxide solution for 15 min at 70 ± 5 °C, and $A$ is the surface area of the phosphated sample.

**Table 1.** Chemical composition of the mild steel substrate

| Element | Composition (wt. %) |
|---|---|
| C | 0.16 |
| Al | 0.07 |
| Si | 0.168 |
| Mn | 0.18 |
| P | 0.025 |
| Cu | 0.09 |
| Fe | balance |

**Table 2.** Operating conditions and chemical composition of the phosphating bath

| Bath composition | (g/L) | Operating conditions |
|---|---|---|
| $H_3PO_4$ (85%) | 15 | T = 55 °C<br>pH = 2.7 |
| ZnO | 1.25 ~ 10 | |
| $HNO_3$ (65%) | 25 | |
| NaF | 0.66 | |

## 2.2. Characterization of Phosphate Coating

The surface morphology and chemical composition of the phosphate coating were assessed by SEM using a Zeiss Supra Model 35VP and EDS. The corrosion resistance of the phosphated substrates was evaluated by immersion test and salt spray test. In the immersion test, the samples were totally immersed in a 3.5% sodium chloride solution and observed after 24 h and 72 h of immersion for discoloration of the solution and the loss in sample weight. The salt spray test was conducted to evaluate the ability of phosphate coatings to prevent underfilm corrosion [18]. Before performing the test, the bare steel and phosphated steels were painted with commercial paint (Uni Paint Factory, white color). The edges of painted samples were sealed with transparent tap to avoid the excessive corrosion at the edges. The coated substrates were scribed to the base metal with a sharp needle so that the base metal is exposed to the salt mist of 5% sodium chloride solution in a salt spray chamber (ASTM B 117-03). The breadth of corrosion from the 'X'-scribe after 48 h of exposure was assessed and photographed.

## 3. Results and Discussion

## 3.1. Coating Morphology and Composition

The SEM micrographs and EDS for zinc phosphate layers obtained by phosphating solutions containing different amounts of ZnO are presented in Fig. 2. SEM result clearly indicated that the rate of coating deposition was markedly increased as the zinc oxide content increased. Almost fully covered coating on the metal substrate was obtained with zinc oxide content of 10 g/L, as depicted in Fig 2(d). This also was confirmed by EDS results which indicated high amount of coating species (especially for Zn and P) was deposited with high zinc oxide content in the phosphating solution. It could be concluded that high number of zinc-metal ions in the phosphating solution has facilitated the precipitation of insoluble zinc phosphates and increased coating coverage. The deposition of zinc phosphate coating was driven by the increase of local pH at metal-bath interface to the basic range. The increase in pH at metal-bath interface was due to the hydrogen evolution at micro cathodic sites [19-20], as shown in Fig 1. During the initial period of the phosphating process, many phosphate crystals were deposited on the metal surface, which continued to grow up until the metal surface was covered by the coating deposition. This film growth is strongly affected by the content of $Zn^{2+}$ in the phosphating solution. High content of $Zn^{2+}$ caused an increase in deposition of insoluble zinc phosphate which led to produce coating with bigger crystal size.

## 3.2. Phosphate Coating Weight

The dependence of phosphate coating weights on the zinc oxide concentration is presented in Fig. 1. It is evident that as the concentration of zinc oxide was increased, the coating weight values (in $g/m^2$) registered a related increase. The maximum value of coating weight (almost 15 $g/m^2$) was obtained when the zinc oxide content was reached to 10 g/L. This high coating weight was due to the high concentration of zinc ions in the phosphating bath which favored high zinc-phosphate formation. In spite of that, with an excessive deposition in the coating formation, the performance of coating adhesion to subsequent organic layers would show an inferior result [21]. Hence, underfilm corrosion behavior was studied by salt spray test as indicated in Fig. 4.

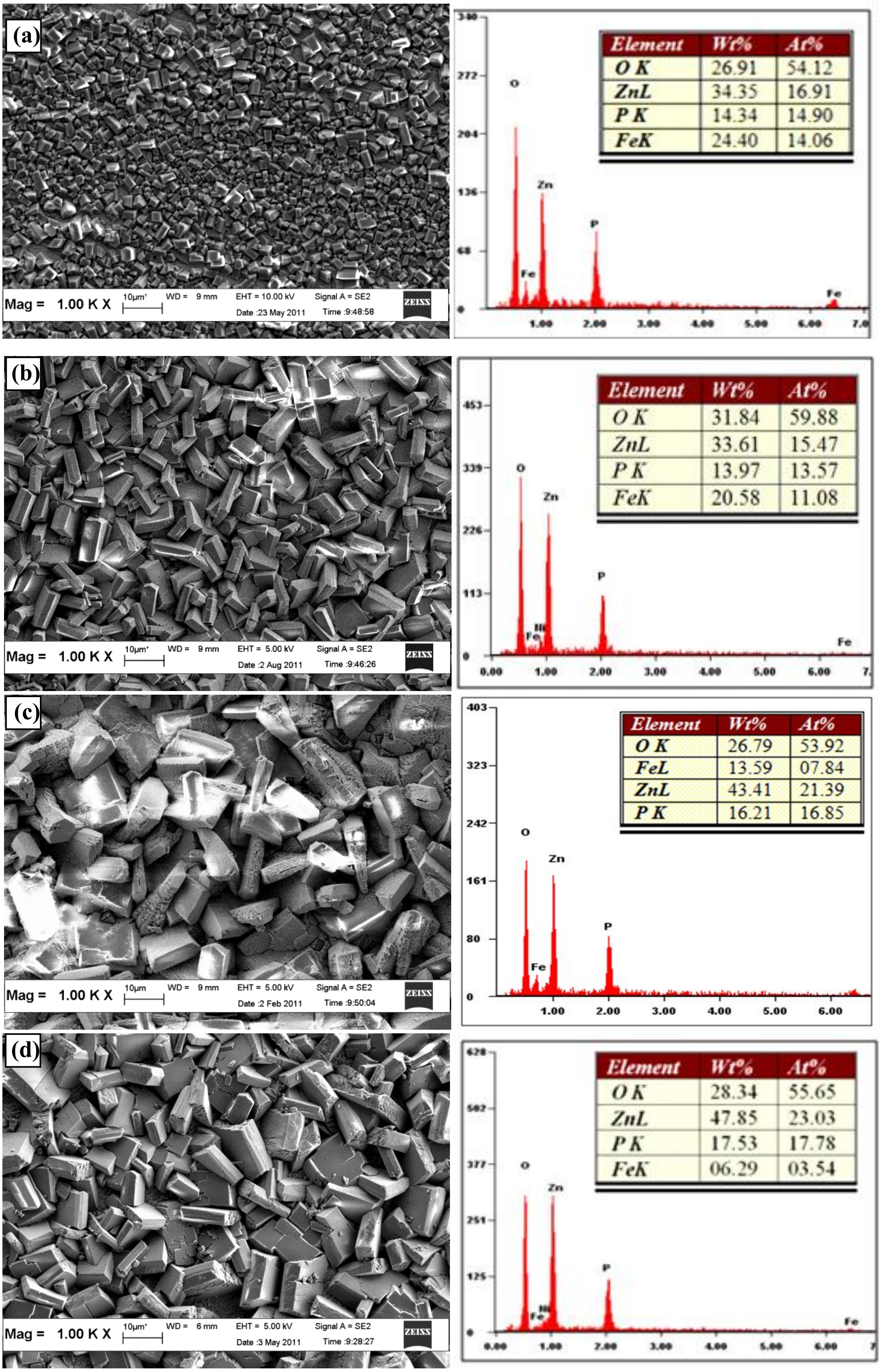


**Figure 2.** SEM micrographs and EDS of phosphated samples with phosphating bath containing various amount of ZnO: (a) 1.25 g/L, (b) 2.5 g/L, (c) 5 g/L and (d) 10 g/L

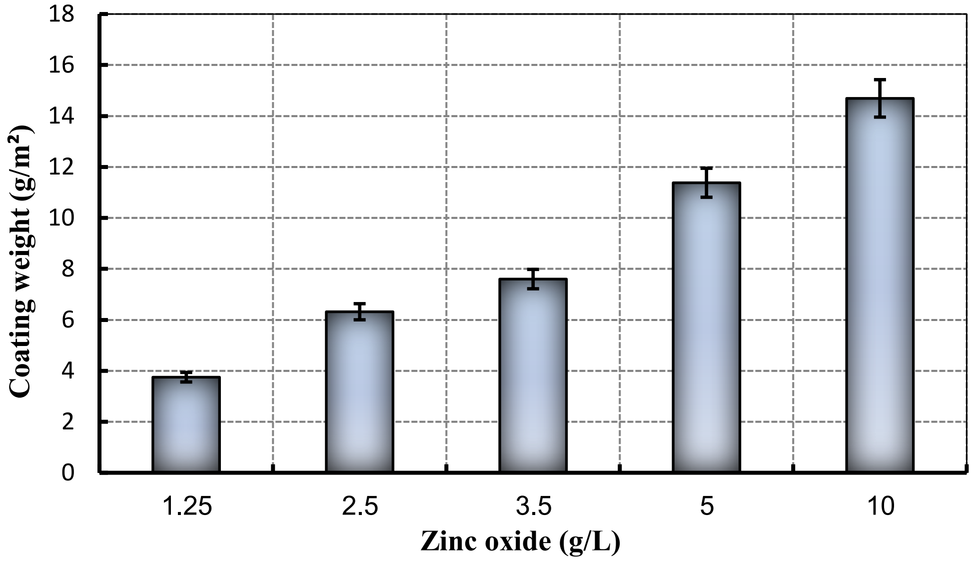


**Figure 3**. Variation of the phosphate coating weights obtained from phosphating solutions with different zinc oxide concentrations

### 3.3. Corrosion Resistance Evaluated by Immersion Test

Immersion test in a 3.5% NaCl solution provides an insight into the corrosion behavior of coated samples. The progress of corrosion is assessed by gravimetric analysis of all specimens due to corrosion after 24 and 72 h of immersion and by visual observation after immersion [22]; as presented in Table 3. Visual observation of various specimens after 24 h revealed that the layers obtained with phosphating solution containing 10 g/l of zinc oxide remained in a good condition and with slight discoloration of the solution. However, discoloration of the solution was observed after 24 h in the case of phosphated substrates obtained with zinc oxide content less than 10 g/L, especially at 1.25 and 2.5 g/l, indicating a higher amount of iron dissolution. The discoloration of the solution was due to the reddish-brown color of ferric hydroxide formed due to the hydrolysis of iron chloride. This iron chloride was resulted from the attack of chloride ions on the pores places of phosphated mild steel substrate [23].

The weight loss determinations were also consistent with the visual observation, where the weight loss of the coated sample was decreased as the zinc oxide content increased. It registered a minimum value of +0.991 and 2.97 g/m$^2$ after 24 and 72 h respectively, when the zinc oxide content was 10 g/L. This suggests that excellent protection ability can be provided by high phosphate coating deposition which serves as a physical barrier between metal surface and corrosive environment.

### 3.4. Corrosion Resistance Assessed by Salt Spray Test

It has been known that, the best method to measure the ability of preventing underfilm corrosion is by assessing the spreading of corrosion from the ‘X’-scribe (scribed to the base metal) made on the painted substrate and subjected to salt spray test [24]. The performance of various painted substrates subjected to salt spray test in 5 % NaCl is presented in Fig. 4. Compared to phosphated steel, the anticorrosive protection was very poor for unphosphated steel. A lot of red rusts were observed on the surface of unphosphated sample after 48 h of salt spray test, as shown in Fig. 4(a). This demonstrates the effectiveness of phosphate coatings in resisting alkaline attack. In the process of salt spray test, the chloride ions have the ability to penetrate the steel surface and reacting with iron to form iron chloride which upon hydrolysis produces the red rust at exposed area of steel surface in the scribed region (anodic areas) [24].

When the zinc oxide content was increased in the phosphating bath from 3.5 to 10 g/L, the spreading of corrosion and paint blistering on the surface of phosphated samples were relatively increased. This indicated that high zinc ion content in the phosphating bath produced coatings with less effectiveness in resisting alkaline attack. This could be attributed to the thick and heavy coating resulted from using high content of zinc oxide, as evidenced by SEM result and coating weight analysis (Fig. 2 and Fig. 3). It is expected that, phosphating solutions with high zinc oxide content will produce zinc-metallic deposition on metal surface with a simultaneous zinc phosphate deposition. This led to inferior underfilm corrosion of the obtained coating due to the preferential dissolution of metallic zinc presented in the coating [18].

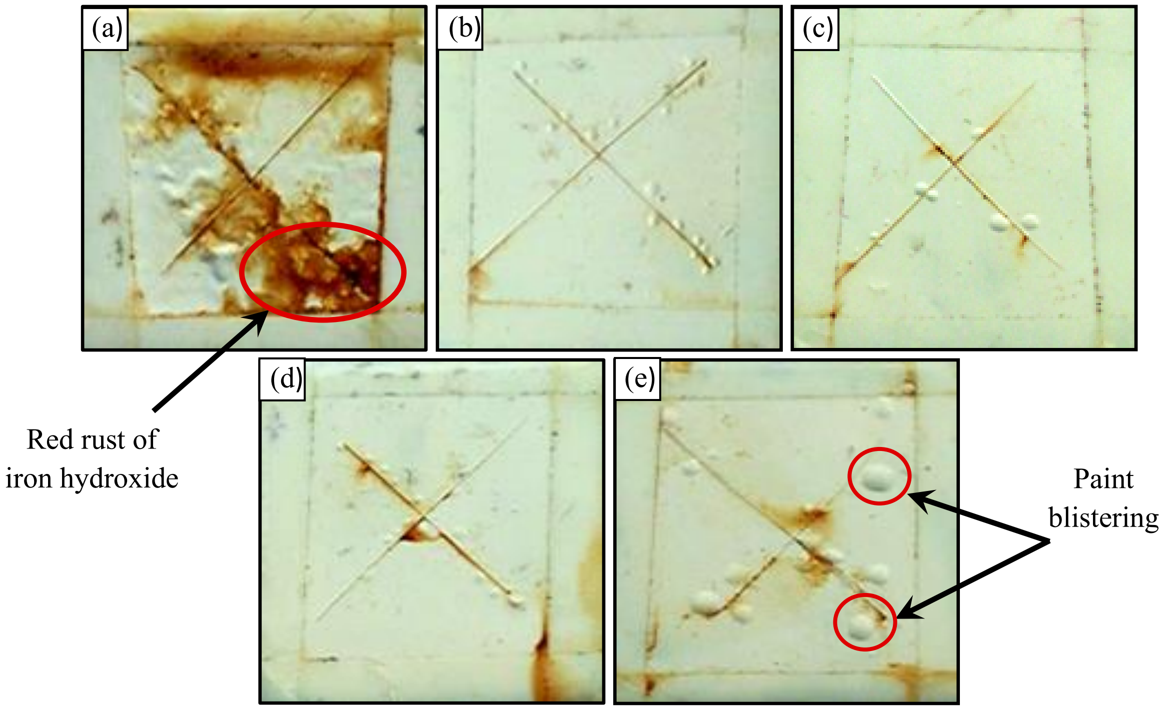


**Figure 4**. Performance of painted mild steel substrates after 48 h of salt spray test of (a) unphosphated steel; and phosphated mild steel with phosphating bath containing various amount of ZnO: (b) 2.5 g/L, (c) 3.5 g/L, (d) 5 g/L, and (e) 10 g/L

**Table 3**. Corrosion resistance of phosphated substrates evaluated by immersion test

| Phosphated substrate | Mass loss after 24 h ($g/m^2$) | Observation after 24 h | Mass loss after 72 h ($g/m^2$) | Observation after 72 h |
|---|---|---|---|---|
| Phosphating solution containing 1.25 g/l of ZnO | 2.35 | Discoloration of the solution | 6.49 | Discoloration of the solution |
| Phosphating solution containing 2.5 g/l of ZnO | 2.10 | Discoloration of the solution | 5.85 | Discoloration of the solution |
| Phosphating solution containing 5 g/l of ZnO | 1.75 | Discoloration of the solution | 3.92 | Discoloration of the solution |
| Phosphating solution containing 10 g/l of ZnO | 0.991 | Slight discoloration of the solution | 2.97 | Discoloration of the solution |

## 4. Conclusions

The effect of zinc oxide in zinc phosphate coatings in terms of coating morphology, chemical analysis, and anticorrosion performance has been studied. It is confirmed that the coating coverage and deposition have improved significantly as the zinc oxide increased in the phosphate solution. Consequently, the weight loss test demonstrated higher corrosion performance of coated samples with increasing the zinc oxide. However, underfilm corrosion test showed inferior corrosion properties of coating produced with high concentrations of zinc oxide in the phosphating solution (over 3.5 g/L). Hence this study concludes that, for phosphate coatings used as a final finish the high zinc phosphating (5 to 10 g/L) is recommended and for phosphate coatings used as a pretreatment coating specially for painting finishes the low phosphating process is recommended.

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