Effect of phosphate coatings on the performance of epoxy polyamide red oxide primer on galvanized steel

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Abstract

Conversion coatings on metals enhance paint or lacquer adhesion and promote corrosion resistance. Present study characterizes three different phosphate baths of zinc phosphate, calcium modified and manganese-modified formulations. It has been observed that manganese modified baths have shown better performance than the other two. The phosphated substrates were coated with epoxy coatings. The coated panels were examined for adhesion by pull off methods and corrosion resistant properties were evaluated by salt spray exposure studies. The electrochemical impedance behaviour of these specimens were also carried out and found that the coatings over phosphate surface performed well compared to these with base metal alone. SEM studies were also conducted to see the surface morphology of the phosphated surface.
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1. Introduction

Phosphating of metal surface is widely used to improve paint adhesion, corrosion resistance, and lubrication and to provide electrical insulation. The phosphating process involves dissolution of a base metal in an acidic solution of soluble primary phosphates with the subsequent hydrolysis of these phosphates and the precipitation of insoluble tertiary phosphates. Phosphate baths for mild steel and zinc usually contain cations of Fe^{2+}, Zn^{2+}, and Mn^{2+}, hence the tertiary phosphates of these are the most constituents of the phosphate coatings. The main function of the protective organic coating is to prevent the corrosion of metal substrates. New coatings are developed that may more effectively withstand in many aggressive environments in which metallic materials are exposed during operation. This evaluation is possible by using electrochemical impedance spectroscopy. Electrochemical impedance spectroscopy [EIS] is a useful method to study the corrosion performance of polymer coated metals [1–3].Many examples can be found in the literature, which illustrate the use of EIS for comparing the performance of different coatings on metals [4–7]. However the use of EIS

to study the effect of pretreatment on the performance of the entire system of metal/pretreatment coating has only rarely been published [8–11]. The general mechanism for coating degradation and substrate corrosion is characterized by an increase in electrolyte uptake, the development of microscopic porosity, and an increase in the ionic conductance in the coating followed by corrosion at the coating–metal interface. [12]. In the course of several years many pretreatments have been investigated to improve the adhesion of polymer to the metal surfaces. The adhesion of polymers depends on the characterization of the metal surfaces, which include surface roughness, surface contaminants, nature of chemical bonds on the surface etc [13].

2. Experimental

Galvanized steel (GS) specimens were used for application of different types of phosphate coatings. GS panels of 75 mm × 50 mm were used for the experiments. Degreasing was effected with trichloroethylene, and then the panels were pickled in 2.5% Tri sodium phosphate solutions at 75 °C for 10 min followed by rinsing in running water and then with distilled water, subsequently etching the surface with 2% H_2SO_4

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acid for 1 min prior to the conversion coating process. Conversion coating treatment was carried out in different bath compositions by immersing the specimens.

2.1. Bath formulations

Zinc phosphate bath		Manganese modified bath		Calcium modified bath	
ZnO	−5 g/l	ZnO	−5g/l	ZnO	−5g/l
H_3PO_4	−12 ml/l	H_3PO_4	−10–15 ml/l	H_3PO_4	−20–25 ml/l
$NaNO_3$	−6 g/l	$Mn_3(PO_4)_2$	−2 g/l	$Ca(OH)_2$	−2 g/l
NaF	−0.3 g/l	$NaNO_3$	−5.5 g/l	$NaNO_3$	−10 g/l
–	–	NaF	−0.3 g/l	NaF	−0.3 g/l

After phosphating, the panels were dipped in distilled water and they were allowed to dry in a stream of hot air at 323–333 K. The coating thickness on galvanized iron surfaces were measured with an Electrophysik, minitest 600FN.Then a epoxy polyamide red oxide primer coating of 50 μm thickness was given on all the treated surfaces of Galvanized iron and cured at room temperature for 21 days.

Salt spray exposure test was conducted as per the ASTM B 117. The panels were inspected at periodic intervals and assigned a ranking based on visual appearance. For EIS measurements, glass tubes were mounted on coated panels in order to expose an area of 1 cm². Then 3% NaCl solution was added to the glass tube. During measurements platinum foil and saturated calomel electrodes were placed in the glass tube containing 3% NaCl solution. The frequency range lies between 10^4 Hz and 10^{-1} MHz using a sinusoidal voltage modulation <20 mV. PAR model 6310 impedance analyzer was used for this experiment. The pull off test was conducted on GI surface and phosphate pretreated with organic coated GI surface using Tensometer 20 Model's. SEM studies were carried out on the above system using HITACHI S 3000H model. In this paper, attempts have been made to correlate the results of EIS with the effect of epoxy polyamide red oxide primer applied on phosphate pretreatment on galvanized steel surfaces. The corrosion characteristics of the coatings were investigated through immersion tests performed in 3% NaCl solution, salt spray test and the impedance data were analyzed in terms of time dependency of characteristic parameters.

3. Results and discussions

Figs. 1–6 show that the Bode impedance plot obtained for the pretreatment and painted GS surface during immersion in 3% NaCl at different exposure times. To determine the influence of the surface preparation, we have to compare the spectrum of the samples to identify the stages of deterioration. The electrochemical behavior of epoxy polyamide coating on GS surface depends on the thickness of the applied polymeric film. In the first hour, after immersion in 3% NaCl solution the impedance diagram is highly capacitive with all the investigated frequency range. After 24 h the impedance values are decreased in all the specimens due to certain elec-

trochemical process taking place along the interface between the coatings and the substrate. After 7 days of exposure it is observed that the impedance of barrier type conversion coatings which can be attributed to the process of ions/water transport through the primer. The impedance values for the coating system (Z) were in the range of 6×10^5, 5×10^6 and 2×10^8 Ω cm² for control GS, zinc phosphate, and calcium modified phosphate respectively. The manganese modified system exhibit a little increase in the frequency range from 5×10^7 to 1×10^8 Ω cm² after 7 days due to the formation of protective phosphate passive layer between the interfacial and the coated substratum.

Haruyama and Asari [14] supported the degradation effect of the coated specimens. The effect was highly related with delaminated area of the coated specimens. Other than manganese modified, all the systems exhibit a decrease in the impedance values. The manganese modified phosphate system with organic coating has a resistance range more than one order of magnitude higher than the calcium modified and zinc phosphate coating system. On the contrary, there is a marginal increase in impedance values after 15 and 30 days
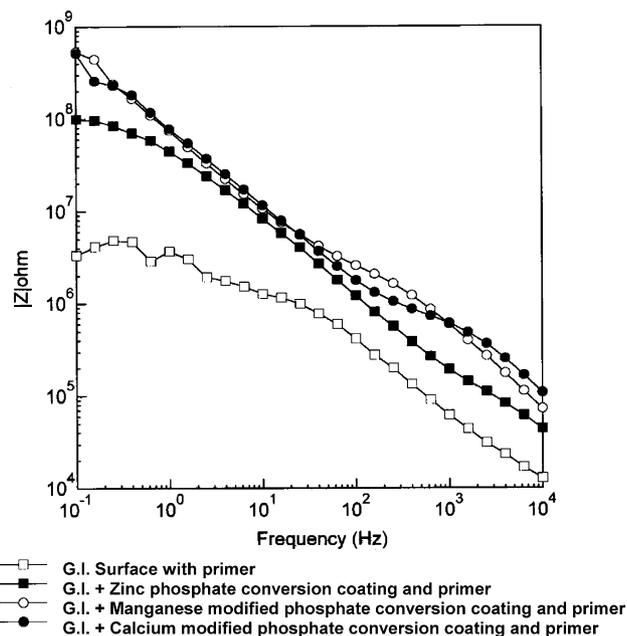

Fig. 1. Bode plots of GI surface with different conversion coatings and primer in 3% Nacl solution for 1 h duration. (□) GI surface with primer, (■) GI + zinc phosphate conversion coating and primer, (○) GI + manganese modified phosphate conversion coating and primer, (●) GI + calcium modified phosphate conversion coating and primer.
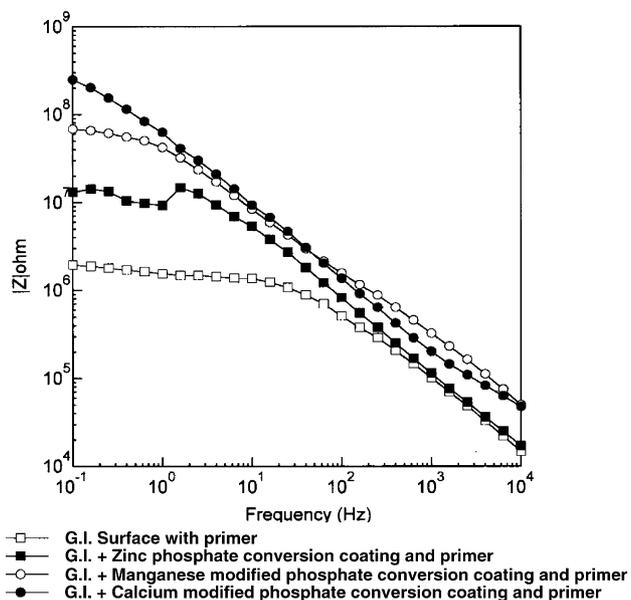
Fig. 2. Bode plots of GI surface with different conversion coatings and primer in 3% Nacl solution after one day immersion. (□) GI surface with primer, (■) GI + zinc phosphate conversion coating and primer, (○) GI + manganese modified phosphate conversion coating and primer, (●) GI + calcium modified phosphate conversion coating and primer.

of exposure in 3% NaCl solution. This could be due to the precipitation of insoluble tertiary phosphates [15]. It is highly evident from the SEM studies that Mn^{2+} in manganese modified phosphate bath is effectively incorporated into the crystal structure. Thus from the above observation it is concluded
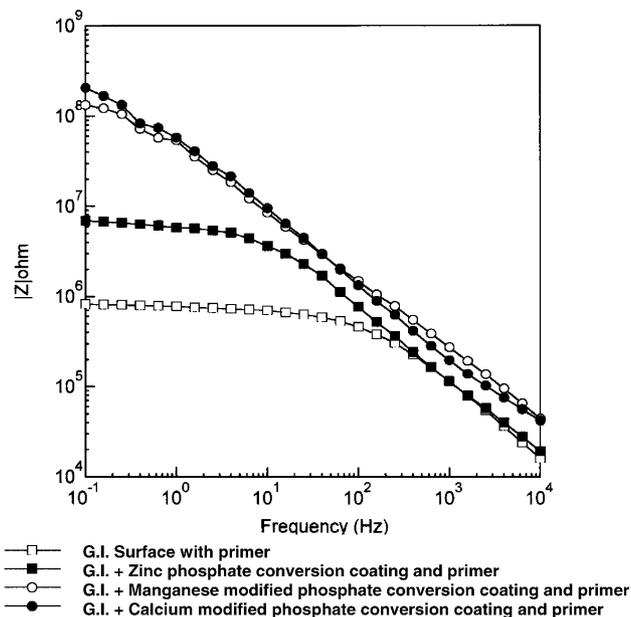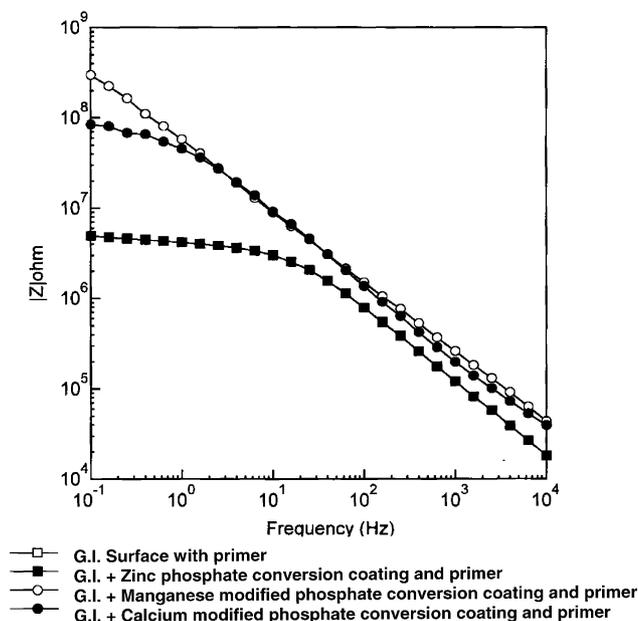

Fig. 4. Bode plots of GI surface with different conversion coatings and primer in 3% Nacl solution after 15 days immersion. (□) GI surface with primer, (■) GI + zinc phosphate conversion coating and primer, (○) GI + manganese modified phosphate conversion coating and primer, (●) GI + calcium modified phosphate conversion coating and primer.

that manganese modified phosphate bath provided acceptable coatings on zinc plated and galvanized surfaces and further it clearly shows the inhibitive nature of the phosphate bath, which is evident from the resistance range of 3×10^8, and $1.5 \times 10^8 \, \Omega \, cm^2$ for 15 and 30 days, respectively. But in the case

Fig. 3. Bode plots of GI surface with different conversion coating and primer in 3% Nacl solution after 7 days immersion. (□) GI surface with primer, (■) GI + zinc phosphate conversion coating and primer, (○) GI + manganese modified phosphate conversion coating and primer, (●) GI + calcium modified phosphate conversion coating and primer.
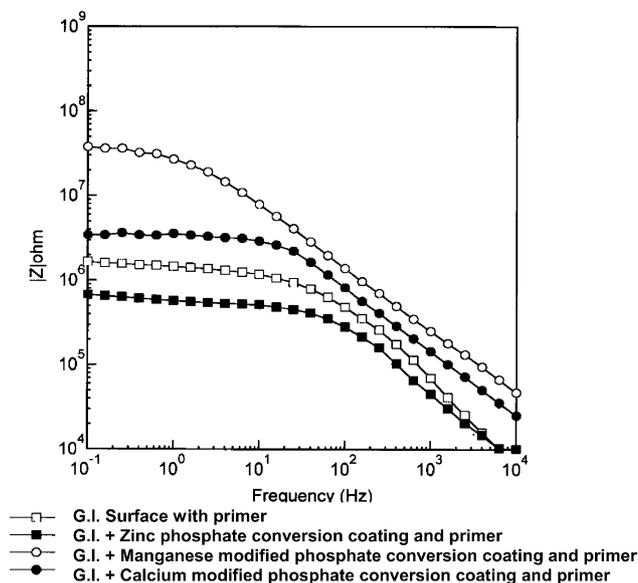

Fig. 5. . Body plots of GI surface with different conversion coatings and primer in 3% Nacl solution after 30 days immersion. (□) GI surface with primer, (■) GI + zinc phosphate conversion coating and primer, (○) GI + manganese modified phosphate conversion coating and primer, (●) GI + calcium modified phosphate conversion coating and primer.
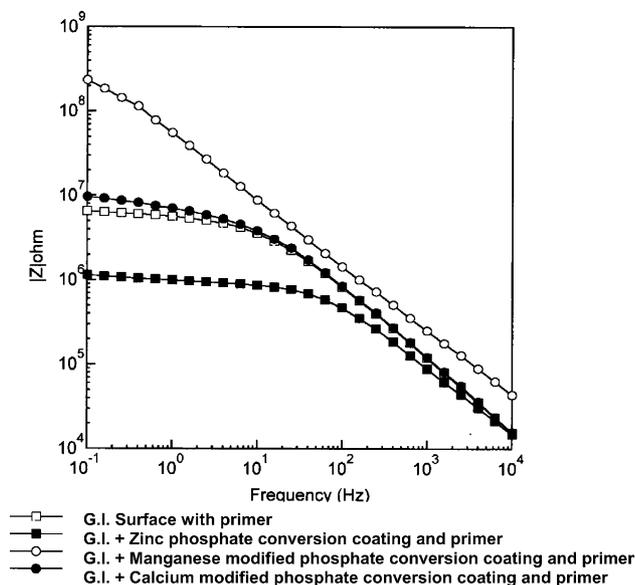
Fig. 6. Body plots of GI surface with different conversion coatings and primer in 3% Nacl solution after 50 days immersion. (□) GI surface with primer, (■) GI + zinc phosphate conversion coating and primer, (○) GI + manganese modified phosphate conversion coating and primer, (●) GI + calcium modified phosphate conversion coating and primer.

of 50 days of exposure there is a sudden fall of impedance values to $3 \times 10^7 \, \Omega \, cm^2$ that may be due to dissolution of phosphate coatings by the complexing effect of phosphate anions. In overall trends, manganese modified phosphate bath exhibit better performance both in the impedance and salt spray tests.

3.1. Salt spray tests

Results obtained after 720 h exposure indicates the absence of white corrosion products on manganese modified primer coated specimens, calcium modified and zinc phosphate systems. Conversion coatings alone based on zinc, calcium and manganese lasted for 8, 48 and 72 h, respectively.

3.2. SEM

Figs. 7–10 summarizes the surface morphology studies on GS surface and phosphated GS surfaces. It is observed from the figures detained that the calcium modified phosphate coatings are uniformly distributed throughout the surface and pattern of deposit is dendrite in nature. The average length of the needle structure is of the order of 20 microns. However in the zinc phosphate coating system the coating is non-uniform and randomly distributed on the GS surface. The grains are spherical in nature, moreover the deposition is found to be selective in nature. The manganese modified phosphate system exhibits the combination of needle and spheroid structures that is distributed uniformly throughout the surface. This particular coating exhibited better corrosion protection compared to other sys-
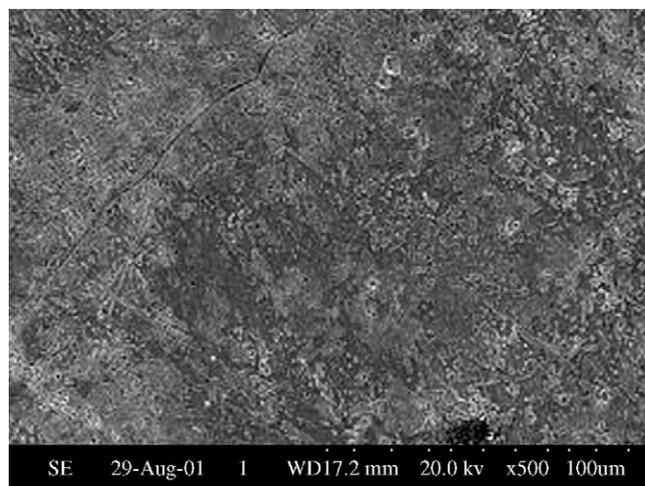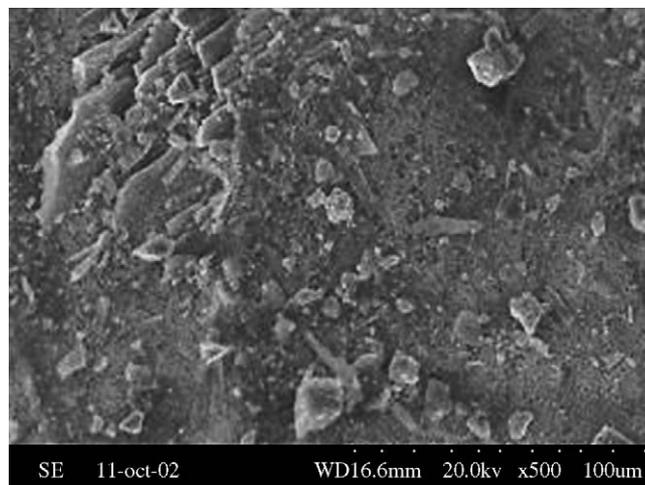

Fig. 7. SEM photograph on GI surface.

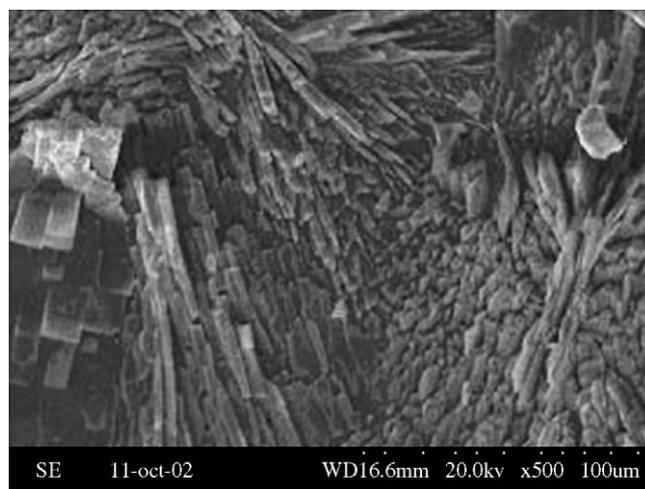Fig. 8. SEM photograph on zinc phosphated GI surface.

Fig. 9. SEM photograph on manganese modified zinc phosphate GI surface.

Table 1
Adhesion values of organic coatings on different conversion coated surface

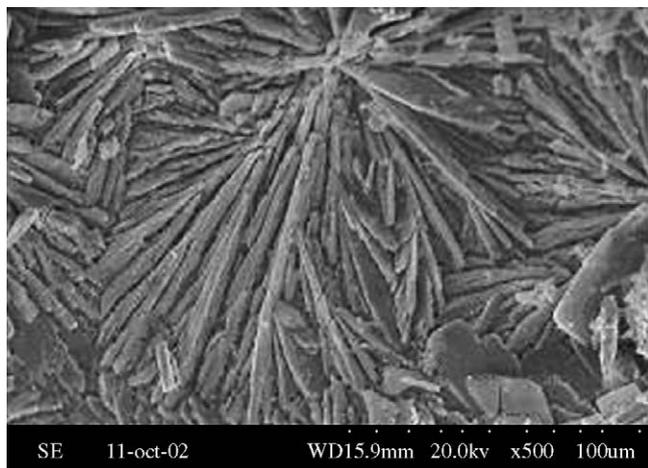| Sl. no.	Surface pretreatment	(N/mm^2)
1	GS surface-alkaline cleaning with acid etchings	4.125
2	ZnO: 5 g/l, H_3PO_4: 12 ml/l, $NaNO_3$: 6 g/l, NaF: 0.3 g/l	4.462
3	ZnO: 5 g/l, H_3PO_4: 25 ml/l, $NaNO_3$: 10 g/l, $Ca(OH)_2$: 2 g/l, NaF: 0.3 g/l	5.384
4	ZnO: 5 g/l, H_3PO_4: 11 ml/l, $Mn_3(PO_4)_2$: 2 g/l, $NaNO_3$: 5.5 g/l, NaF: 0.3 g/l	5.81

Fig. 10. SEM photograph on calcium modified zinc phosphate GI surface.

tems, which may be due to the reduction of porosity and roughness.

3.3. Adhesion

Table 1 summarizes the adhesion values of epoxy polyamide red oxide primer coating on different phosphate coatings. One of the most important factors for adhesion of coating material to the substrate is its stability when exposed to water or high humidity. It is observed from the tests, that zinc phosphate coatings on GS surface gets cohesive failure on the matrix, because of less porous nature. Whereas the manganese modified phosphate coating enhances the adhesion properties due to more porous nature and galvanic action on the GS matrix. Van Ooij et al. [16] supported the improved adhesion properties of the coated specimens in presence of Mn^{2+}. Further it is clearly evident that alkaline cleaning followed by acid etching before conversion coating operation improves the adhesion of organic coating due to removal of strong organic contamination and elimination of oxide layer.

4. Conclusions

1. Surface pretreatment with manganese modified phosphate system on the GI surface is more effective than the calcium modified and zinc phosphate system as far as corrosion protection is concerned.
2. Alkaline cleaning with acid etching improves the adhesion of organic coatings due to removal of strong organic contaminations and alteration of oxide layer.
3. Manganese addition to the phosphating bath enhances adhesion properties compared to calcium addition and zinc phosphate bath.
4. SEM studies show that the nature of deposits is non-uniform in the zinc phosphate system and it is uniform in the calcium modified and manganese modified phosphate system.

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