Performance and Characterization Study of Zinc Phosphate Coating over Steel for Automotive Application

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Abstract: Zinc phosphate coating has recently been paid much attention. Under the specified conditions of the selected anti-corrosion resin, is a function pigment is key to improving the anticorrosive properties of the coating. Zinc phosphate is an effective anti-corrosion and environmental protection pigment. In this work, zinc phosphate was used to modify the level of oxide in the coatings. In addition, the peel resistance of the coating was studied. The coated specimens were examined for corrosion resistant properties were evaluated by salt spray exposure studies. SEM studies were conjointly conducted to ascertain the surface morphology of the phosphated surface.

1. Introduction

Continuous environment issues have directed attention toward $Zn_3(PO_4)_2$ coatings. Phosphating of metal surface is widely used to improve paint adhesion, corrosion resistance, lubrication and to provide electrical insulation [16]. The phosphating method involves dissolution of a base metal in associate in nursing acidic resolution of soluble primary phosphates with the following chemical reaction of those phosphates and also the precipitation of insoluble tertiary phosphates [18]. Thus, spray coatings need to have improved performance for long-term applications. Spray coatings have good barrier properties and ageing resistance, which has attracted much attention [3]. The zinc phosphate coating is formed by crystallization on the surface through a chemical reaction [15]. The zinc phosphating should be applied by spray or dip and it should can be used for any phosphating application [20]. Scanning electron microscopy (SEM) has appeared that exceptionally fine zinc particles encompassed phosphate gems and filled within the interstice of the insoluble phosphate [20]. Phosphate baths for mild steel and zinc generally contain Fe^{2+}, Zn^{2+} and Mn^{2+} cations, therefore their tertiary phosphates are the most important components of phosphate coatings [7]. The addition of a type of oxide active antioxidant pigment is a common method to improve the antioxidant capacity of the coating [3]. Many pre-treatments have been explored over the years to improve polymer adhesion to metal surfaces [19]. Much attention has been paid to phosphate antirust pigments because of their relative environmental friendliness [19],[17]. The antirust function and mechanism of zinc phosphate have been studied previously [18]. Phosphate pigments mainly contain aluminum tripolyphosphate and zinc phosphate. Polymer's adhesion depends on the characterization of metal surfaces, including surface roughness, surface contamination, type of chemical bonds on the surface, etc.

2. Experimental

The substrate material used in this study was mild steel with the specimen size of 90×70×5 mm. The main compositions are MgO, ZnO, sodium fluoride and other additives like H_3PO_4, H_2O and $C_{10}H_{16}$. Degreasing was affected with trichloroethylene, then the panels were preserved in 2.5% Tri sodium phosphate solutions at 75 ∘ C for 10 min followed by removal in running water and then with distilled water, after etching the surface with 2% H_2SO acid for one min before the conversion coating process. Conversion coating treatment was meted out in numerous both compositions by immersing the specimens.

In the present phosphating bath, ZnO and H_3PO_4 is that the main coating form substances. the subsequent reactions would possibly occur within the bath contained ZnO and H_3PO_4: $ZnO+H_3PO_4+H_2O \rightarrow Zn(H_2PO_4)_2 \cdot 2H_2O$.

The presentation $Zn(H_2PO_4)\cdot 2H_2O$ of the reaction (1) is soluble, it dissolved in the phosphating bath to provide $ZnPO_4^-$, $H_2PO_4^-$, H^+ and H_2O: $Zn(H_2PO_4)_2\cdot 2H_2O \rightarrow ZnPO_4^- + H_2PO_4^- + 2H_2O$. The complex ion $ZnPO_4^-$ has the ionization reaction as follows: $ZnPO_4^- \leftrightarrow Zn^{2+} + PO_4^{3-}$.

2.1 Materials and methods:

The substrate material used in this study was mild steel with the specimen size of 90×70×5 mm. A composite coating composed of 8 % zinc phosphate will be prepared by high-speed shearing mixing, The zinc phosphate was dried for 15 min at 50 ∘C, and then the film-forming agent, wetting dispersant, flash rust agent, zinc phosphate, and a certain amount of water were added successively, after adding the above fillers, the solution was manually stirred using a glass rod for approximately 10 min and then dispersed using a high-speed shearing dispersion machine for 30 min [17]. To obtain powder form of an MS specimen, The specimen must rub with Silicon carbide waterproof paper on the corroded surface area. After rubbing, you will achieve silicon carbide powder form. The MS surface must be cleaned with $NaHCO_3$ (sodium bicarbonate). $NaHCO_3$ will expels the corrode powder from the specimen surface.

2.1.1 Methodology

To obtain powder form of an MS specimen, you must rub it with Silicon carbide waterproof paper (grade E4) on the corroded surface area. After rubbing, you will achieve silicon carbide powder form, The MS surface must be cleaned with $NaHCO_3$ (sodium bicarbonate) [15]. $NaHCO_3$ will expels the corrode powder from the specimen surface. Before cleaning with $NaHCO_3$, clean the MS surface with air dryer to remove corrode powder from the MS surface, and then dried, the above coating was sprayed and brushed with different metal specimens into different layers, The coating thickness of the specimen used for Adhesion test, SEM image was 0.16 ± 0.02mm, the coating was dried for 3 days at room temperature, and the adhesion test was carried out with a tool knife made of LB30N steel.

2.1.1.1 Abrasive

To obtain powder form of an MS specimen, you must rub it with Silicon carbide waterproof paper (grade E4) on the corroded surface area. After rubbing, you will achieve silicon carbide powder form.

2.1.1.2 NaHCO3 surface cleaning

The MS surface must be cleaned with $NaHCO_3$ (sodium bicarbonate). $NaHCO_3$ will expels the corrode powder from the specimen surface. Before cleaning with $NaHCO_3$, clean the MS surface with air dryer to remove corrode powder from the MS surface.

2.1.1.3 Zn3(PO4)2 coating

Chemical Composition	ZnO	5g/L
	H_3PO_4	11.3mL/L
	$NaNO_2$	2 g/L
Control parameters	pH	2.70
	Free acid value (FA) pointage	3 pointage
	Total Acid value (TA) pointage	25 pointage
	FA: TA	1: 8.33

Operation condition	Temperature	27*c
	Time	30 min

2.1.1.4 Method of coating

The zinc phosphate coating is formed by crystallization on the surface of a substrate. Zinc phosphating can be applied by spray or immersion, and it can be used for all phosphating applications. Spray coating on steel surfaces ranges in weight from 1–11 grams per square meter, and immersion coating ranges from 1.6–43 grams per square meter.

2.1.1.5 Drying process

A composite coating composed of zinc phosphate will be prepared by high-speed shearing mixing, and the coated zinc phosphate will be dried for 15 minutes at 50°C.

3. Results

3.1 The Coating Adhesion Test

Adhesion values of 0% and 8% zinc phosphate coatings. Adhesion values were the same for the 0% and 8% zinc phosphate coatings. The addition of zinc phosphate did not affect the mechanical performance of the initial coating.

The adhesive fracture in the samples while not and with 8% zinc phosphate coating. The fracture mode for the 8% zinc phosphate coating once the area experiment, that is that the mixture of the coating body and adhesive layer fractures, showed robust adhesion. These results are similar with the sample without zinc phosphate coating, solely the quantitative relation of the coating body and adhesive interlayer fractures is different.

3.2 The Coating Morphology

Figure 1 shows the scanning electron microscope (SEM) section of the 8% zinc phosphate coating. The Zinc phosphate coating has a homogenized dispersion and combined with the resin tightly. Moreover, adding zinc phosphate didn't show defects.

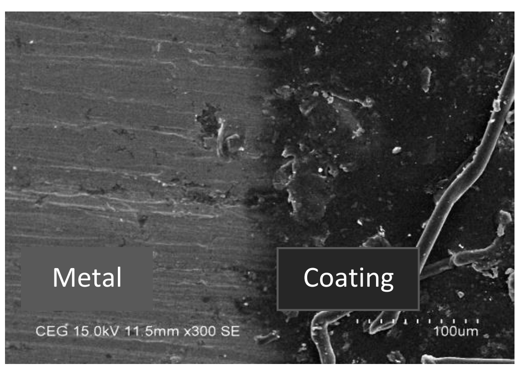


Figure 1. The section morphology of the 8% zinc phosphate coating.

The morphology of the coating without and with 8% zinc phosphate in 4.80-5.30% NaCl solution after various immersion days. At the beginning, the 8% zinc phosphate coating morphologies were the same. However, after a day of immersion, the Zero percentage zinc phosphate coating generated obvious corrosion. The coating generated serious corrosion after five days of immersion, and the defective coating bubbled after seven days. In the 8% zinc phosphate coating, rust occurred after a day of immersion and increased after seven days, but no bubbling was observed.

3.3 ASTM D 6677-01

For Adhesion test ASTM D 6677-01 test is done. The testing is done by making an "X" cut into the specimen, and by lifting the coating with a sharp knife, Adhesion is evaluated on a scale of 0 to 10 where 0 being the worse and 10 being having the best adhesion, note that these results might not be standard and can be differ from person to person. An area is selected on the specimen which is free of blemishes and surface imperfections, and using knife an "X" cut is made, an attempt is made to lift of the coating from the substrate, i.e removing the coating off the surface, and evaluation is done by the difficulty in removing the coating, and it can vary from person to person. The same process is repeated on different surfaces of the specimen to ensure that the adhesion evaluation is representative of the whole surface. From the above test the adhesion rating of spray coating of zinc phosphate using ASTM D 6677 process is given by 4.

3.4 Salt Spray Test

Results obtained after 12h exposure indicates the absence 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 24h, respectively. A salt spray test is a corrosion testing methodology that uses high-saline environments to live the corrosion resistance of products, paints and coatings over extended periods.

Sl. No	Test Parameters	Maintained Values
1.	Chamber temperature	34.5 – 35.5 ∘ C
2.	pH value	6.65 – 6.85
3.	Volume of salt solution collected	1.00 – 1.50 ml/hr
4.	Concentration of solution	4.80 – 5.30% of Nacl
5.	Air pressure	14 – 18 psi
6.	Components loading in the chamber position	30 Degree angle

Observation:

-No rust formation noticed up to 12 Hrs.

-Red rust formation notified at 24 Hrs.

3.5 Scanning electron microscope (SEM)

The SEM images reveal that spray coating of zinc phosphate increases the coating formation and decreases the porosity of the coating. Spray coated specimens are found to be less compact. The spray coating gave smooth deposits with reduced porosity. The SEM images also revealed the coating increased the corrosive resistive properties leaving the properties of the specimen intact, the coating formed a layer around the surface of the specimen, while not reacting with specimen itself, thus not changing the properties of the material.

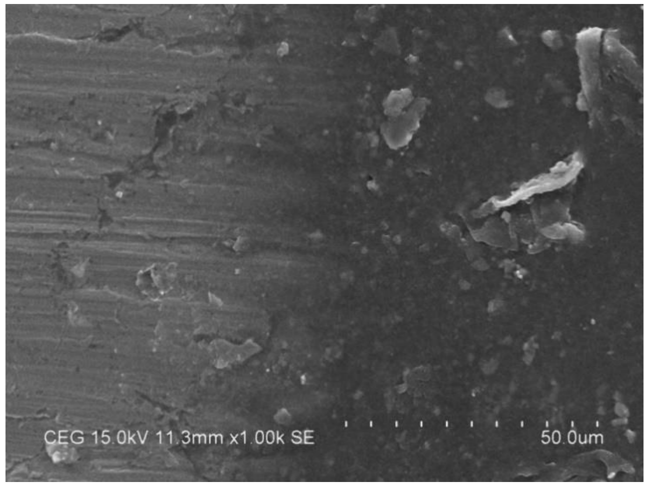


Figure 2. Scanning electron microscope (SEM) comparison of metal surface and $Zn_3(PO_4)_2$ coatings Surface

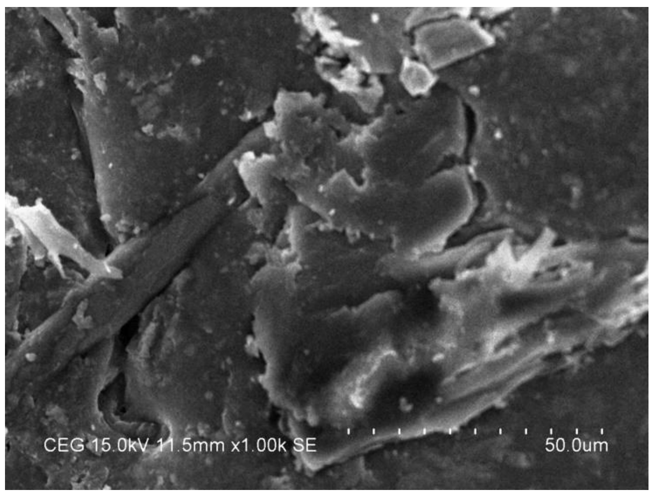


Figure 3. Scanning electron microscope (SEM) comparison of $Zn_3(PO_4)_2$ coatings Surface

Figs. 2-4 summarizes the surface morphology studies on mild steel (MS) surface and phosphated MS surfaces. It is observed from the figures detained that the calcium modified phosphate coatings are similarly distributed throughout the surface and pattern of deposit is dendrite in nature. The average length of structure is of the various of microns. However, in the zinc phosphate coating system the coating is uniformly and randomly distributed on the MS surface. The grains are spherical in nature, that the deposition is found to be selective in nature. The manganese modified phosphate system exhibits the combination of spheroid structures that is distributed uniformly throughout the surface. This particular coating exhibited better corrosion protection compared to all other systems, which might ensue to the reduction of porousness and roughness.

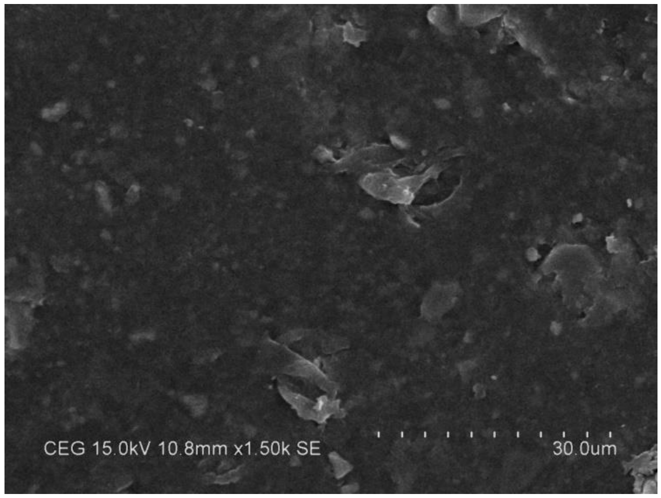


Figure 4. Scanning electron microscope (SEM) comparison of $Zn3(PO4)2$ coatings Surface

3.6 EDX

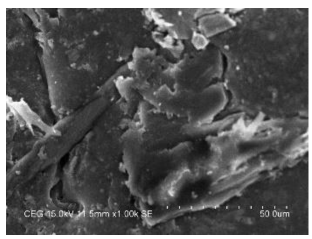
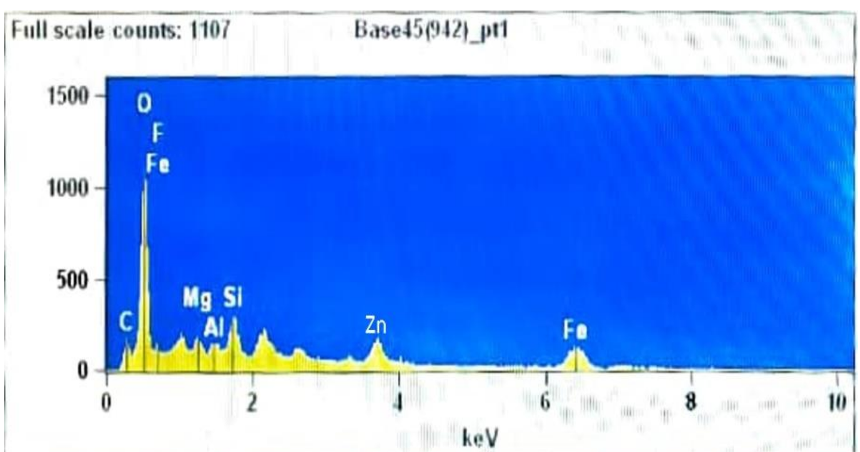


Image Name: Base45(942)

Accelerating Voltage: 15.0 Kv



Net Counts

	C	O	F	Mg	Al	Si	Zn	Fe
Base45(942)_pt1	1120	10405	218	869	907	2984	1574	2252

Weight %

	C	O	F	Mg	Al	Si	Zn	Fe
Base45(942)_pt1	15.74	46.36	2.18	2.23	2.23	6.92	3.57	24.34

Atom %

	C	O	F	Mg	Al	Si	Zn	Fe
Base45(942)_pt1	25.31	55.95	2.21	1.77	1.60	4.75	2.95	8.41

4. Conclusions

1. From the study, it is evident that spray coating of zinc phosphate is capable of producing fine, adherent and corrosion resistance. During the immersion in 5% NaCl solution proved that the spray coating developed is uniform, less porous, efficient, and it exhibited high corrosion resistance.

2. In the adhesion test, the spray coating was hard to remove and it was stably on the surface of the specimen. The fracture mode for the 8% zinc phosphate coating once the area experiment, that is that the mixture of the coating body and adhesive layer fractures, showed robust adhesion.

3. The SEM images revealed the coating formed a layer around the surface of the specimen, while not reacting with specimen itself, thus not changing the properties of the material.

4. Comparing to the other methods of corrosion resistance, spray coating of 8% Zinc phosphate is still a better alternative considering its low cost, corrosion resistance and better adhesion and easy process.

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