



The improvement of anticorrosion properties of zinc-rich organic coating by incorporating surface-modified zinc particle

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ABSTRACT

The corrosion behaviors of zinc-rich coating with various zinc contents, ranging from 0 to 60 volume percent, in thin organic coatings (below 5 μm) were characterized by electrochemical impedance spectroscopy (EIS), free corrosion potential (E_{corr}) measurement and cycle corrosion test (CCT). It was verified that both coatings with 60 volume percent of zinc powder and without zinc powder showed good corrosion resistance mainly due to the cathodic protection and barrier effect, respectively. On the other hand, coatings with an intermediate concentration (10–40 vol.%) of zinc powder was not successful in protecting a steel substrate efficiently. To improve anticorrosion property of zinc-rich coating, the surface modification of zinc particle was carried out with derivatives of phosphoric and phosphonic acid in the aqueous solution. The effects of the surface modification of zinc particle on corrosion resistance of the coating were investigated with scanning vibrating electrode technique (SVET) and X-ray photoelectron spectroscopy (XPS). The best anti-corrosion performance was achieved when the incorporated zinc particle was treated with phosphoric acid 2-ethylhexyl ester and calcium ion simultaneously, which induced the formation of alkyl-phosphate-calcium complex layer of 190 nm in thickness on zinc particles. Corrosion resistance was improved by the decreased zinc activity and the increased compatibility between the formed complex layer on zinc surface and polymer binder matrix.

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1. Introduction

Metal particles are frequently incorporated into coatings on metallic substrates for various purposes. Zinc metal particles have been widely used to improve the corrosion resistance of coatings for more than 50 years [1]. There also have been many studies on zinc-rich organic coatings in order to improve their corrosion resistance. Kalendová [2] and Jagtap et al. [3] studied the effects of size and shape of zinc particles on the properties of anticorrosive coatings. Hare and Kurnas [4] investigated the effect of pigment/binder ratio on the performance of zinc-rich coatings. Kalendová et al. [5] evaluated the efficiency of inorganic nonmetal pigments, such as zinc phosphomolybdate and calcium borosilicate, on the corrosion resistance of zinc-rich coatings. The performance of zinc-rich coatings has improved significantly due to their efforts [6,7].

Another type of zinc-rich coating was introduced in the middle of the 1990s in the automotive industry with the intention of imparting weldability to organic coatings [8]. The steel sheets were joined partly with each other at some sites during assembly into the automobile body. Since such overlapped areas of steel

sheets were difficult to be treated with paint or phosphate solutions, they became highly susceptible to corrosion. As a solution for this problem, cavity wax spray was employed to seal overlapped sites of steel sheets to prevent corrosive factors from approaching the joint sites. However, this method caused low productivity and higher production costs. In consequence, pre-coated steel sheets with paints that allow the welding of coated metal was proposed as an alternative to overcome the problem. Much effort has been invested in improving the corrosion resistance and weldability of the coating by incorporating corrosion inhibitive pigments together with conductive pigment such as iron phosphide (Fe_2P). However, because the size of commercially available inhibitive pigments is usually several microns, the incorporation of these pigments can deteriorate the mechanical properties of the organic coating, particularly in thin film coatings, below 5 μm . In addition, formability, tool wear and tool contamination when iron phosphide was mixed into the coating. Hence, improvement of the current systems without addition of other functional pigments is the most promising strategy. Bastos et al. [9,10] studied the effect of surface modification of zinc powder to improve the corrosion resistance of weldable primers. They tested corrosion inhibitors, of inorganic (cerium and lanthanum nitrates) and of organic nature (benzotriazole and 2-mercaptobenzothiazole), as surface modification materials. However, they concluded that the pre-treatment

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Table 1

Formulations for the solution of surface modification. The solutions were designed based on the formulation of conventional phosphate conversion coating solution [16].

	ZP1	ZP2	ZP3	ZP4
Zn powder	15 g	15 g	15 g	15 g
Water	200 g	200 g	200 g	200 g
Zinc oxide	0.33 g	0.33 g	0.33 g	0.33 g
Sodium nitrite	3 g	3 g	3 g	3 g
Calcium nitrate		2 g		2 g
Phosphoric acid	0.5 M	0.5 M		
2-ethylhexyl ester Amino trimethylene phosphonic acid			0.5 M	0.5 M

of zinc powder with corrosion inhibitors had no significant effect.

In the present work, the corrosion mechanism of zinc-rich coating in thin organic coatings (below 5 μm) was investigated to find out key factors for improving the corrosion resistance. In addition, the cathodic protection ability of zinc-rich coating on a cold-rolled steel substrate was evaluated. Furthermore, in order to improve the anticorrosion property of the coatings, the surface modification of zinc particles was performed by derivatives of phosphoric and phosphonic acid such as phosphoric acid 2-ethylhexyl ester and amino trimethylene phosphonic acid. They have been demonstrated to form a stable protective film on metallic substrates such as iron, aluminum and zinc [11–13]. It also has been demonstrated that the multivalent metal cation, such as Ca^{2+} , Zn^{2+} and Mg^{2+} , can help the formation of a complex insoluble passive layer on the metal surface in the presence of phosphonate complex and carboxylate complexes [14,15]. For investigating the action of the multivalent cation on the formation of passive layer, the calcium ion, Ca^{2+} , was added to the surface modification solution.

2. Experimental

2.1. Surface modification of zinc particles

Zinc particulate used in this study was obtained from SB Chemical Co., Ltd., Korea. The particles were spherical in shape and the particle diameter ranged from 2 to 5 μm . The zinc particles were modified chemically to reduce their electrochemical reactivity. The surface modification was carried out with two different derivatives of phosphoric and phosphonic acid from Tokyo Chemical Industry Co., Ltd., Japan: phosphoric acid 2-ethylhexyl ester (mono- and di-ester mixture) and amino trimethylene phosphonic acid. Calcium nitrate (Daejung Chemicals & Metals co., Ltd., Korea) was used as the calcium ion source of the surface modification solution. Zinc oxide (Samchun Pure Chemical Co., Ltd., Korea) and sodium nitrite (Kanto Chemical Co., Inc., Japan) were also employed in the surface modification solution for the specific reasons as described in Section 3.2. The detailed formulations for the modification solution are listed in Table 1. After blending all chemicals in the water medium except the zinc particles, the solution was stirred using a magnetic stirrer for 10 min. Then, the zinc particles were added quickly and stirred again for 24 h at the room temperature. Zinc particles were recovered by centrifugations and then washed twice with distilled water to remove the residual chemicals around the particles. Lastly, the surface-modified zinc particles were dried in a convection oven at 50 $^{\circ}\text{C}$ for 48 h.

2.2. Preparation of coated steel panels

Zinc-rich coatings with various pigment volume concentrations (PVCs) were prepared by varying the zinc content of the paint formulation. The main ingredients in the formulation were a polyester resin (Skybon ES-910 from SK Chemicals Inc.) and hexa(methoxy methyl) melamine (Cymel 303 from Cytec Industries Inc.). They were mixed in a 1:1.2 stoichiometric ratio. p-Toluenesulfonic acid (p-TSA) (Nacure[®] 2530 from King Industries Specialty Chemicals, USA) was used as a catalyst and di-n-butyl ether, 2-butoxyethanol and cyclohexanone were used as solvents. The coating solution was prepared by a laboratory scale high speed dissolver (Dispermat[®] LC 2, BYK-Gardner, USA). The coating was applied on a cold rolled steel substrate by a bar applicator and then the film was cured at the peak metal temperature (220 $^{\circ}\text{C}$) in a high frequency induction oven. Before the coating application, the steel panel was degreased with acetone and rinsed with distilled water. The dry film thickness of coated panels was about 5–6 μm , which was measured by a portable thickness measurement system (Quanix 8500, Germany).

2.3. Characterization

To evaluate the corrosion resistance, a cyclic corrosion test was performed. The test cycle was carried out as described below:

Salt spray (5% NaCl solution, 10 min) \rightarrow Humid (80% RH, 30 $^{\circ}\text{C}$, 60 min) \rightarrow Drying (50% RH, 40 $^{\circ}\text{C}$, 60 min) \rightarrow Rinsing (10 min) \rightarrow Drying (35% RH, 40 $^{\circ}\text{C}$, 140 min)

In some samples, salt spray test (ASTM B117) was performed. After a certain amount of time had passed, the surface of coated specimen was observed by optical microscopy and evaluated in terms of the corrosion resistance. Furthermore, in order to investigate the cathodic protection ability of zinc rich coatings, free corrosion potential (E_{corr}) measurements were carried out with an EG&G Princeton Applied Research M263A Potentiostat/Galvanostat during immersion in 3.5% NaCl solutions. A three-electrode arrangement, consisting of a saturated calomel reference electrode, a platinum foil as a counter electrode and the exposed sample as a working electrode with a surface area of 13 cm^2 , was used. The electrochemical impedance spectroscopy measurements were also carried out using a Gamry Reference 600 with PCI4 Controller during immersion in 3.5% NaCl solutions. Arrangement of the electrochemical cell for EIS was same with the cell used for corrosion potential measurements. The impedance measurements were performed at an open circuit potential with applied 10 mV sinusoidal perturbations in the frequency range of 10^{-2} – 10^5 Hz with 10 steps per decade. Scanning vibrating electrode technique (SVET) was employed to measure the current distribution in the surface of the zinc electrodes or coated specimens. The SVET equipment is manufactured by Applicable Electronics Inc. (USA) and controlled by the ASET program (Sciencewares, USA). The microprobes, made of platinum–iridium (Microprobe, Inc., USA), was coated with black platinum deposit of 10–20 μm . The measurements were made with the electrode tip vibrating at 200 μm above the sample surface. The maps were made on 3 mm \times 3 mm area for zinc electrode and 6 mm \times 6 mm area for coated specimen with a matrix of 41 \times 41 points. The surface morphology was observed using scanning electron microscopy (SEM, Hitachi SU-6600). Before SEM observations, the samples were coated by 10 nm of Pt/Pd. X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical composition and thickness of the surface modified thin layers on a zinc electrode. XPS measurements were performed using a VG Scientific ESCALAB 250 system. The analysis area was 20 μm \times 20 μm and the sputter rate was 1.5 nm/min for the first 20 min and then 5 nm/min with Al K α source (1486.8 eV).

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