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Corrosion protection with zinc-rich epoxy paint coatings embedded with various amounts of highly dispersed polypyrrole-deposited alumina monohydrate particles

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ABSTRACT

Active anodic zinc content below 90 wt.% does not support sufficient electrical contacts but higher contents cause high porosity of traditional liquid zinc-rich paints (ZRPs). To resolve this problem, our proposal is the application of highly dispersed polypyrrole (PPy) coated alumina inhibitor particles (PCAIPs) in zinc-rich paint compositions. Using these nano-size inhibitor particles at concentrations from 4.55 to 0.85 wt.%, hybrid paints were formulated with zinc contents ranging from 60 to 85 wt.% at the same time. Submicron morphology and nano-scale structure, spectroscopy characteristics and electrochemical properties of the PCAIPs were studied by transmission electron microscopy (TEM) and rheology, Fourier-transform infrared spectroscopy (FT-IR) and cyclic voltammetry (CV) in first part of the work. In the second part, electrolytic corrosion resistivity of two sets of paint coatings were salt-spray chamber and immersion tested with 5 wt.% aqueous solution of sodium chloride. Active corrosion prevention ability of the salt-spray tested coatings was evaluated in compliance with ISO recommendations. Dielectric properties of the coatings during the immersion tests were monitored by electrochemical impedance spectroscopy (EIS). Corrosion tested area of the coatings was investigated by glow-discharge optical emission spectroscopy (GD-OES) to disclose infiltration of corrosive analytes and oxygen enrichment in the cross-section of the primers in comparison with their pristine states. Morphology of the zinc pigments was examined by scanning electron microscopy (SEM), and quality of steel specimens and the interfacial binder residues by X-ray photoelectron spectroscopy (XPS) as well as FT-Raman and Mössbauer spectroscopy. The results of both types of corrosion tests evidenced efficient utilisation of sacrificial anodic current for galvanic protection and improved barrier profile of the hybrid coatings, along with the PCAIP inhibited moderate self-corrosion of zinc. As a result of well balanced active/passive function, the hybrid coating containing zinc at 80 wt.% and PCAIPs at 1.75 wt.% embedding PPy at 0.056 wt.% indicated the most advanced corrosion prevention. Galvanic function of the hybrid paints is interpreted on the basis of size-range effect and spatial distribution of the alumina supported PPy inhibitor particles and basic electrical percolation model considerations.

1. Introduction

Corrosion protection performance of hitherto extensively investigated liquid ZRPs [1,2] is limited by the electrical and electrolytic conductivity of the primer coatings [3,4]. The former is connected to the electrical percolation phenomena relating to the pigment volume concentration (PVC) and the latter is affected by the porosity of the coatings. Porosity determines accessibility of anodic pigments by the electrolyte, affecting electrical conductivity of the primers as well as the intensity of sacrificial and self-corrosion of the zinc. These factors have a strong impact on the effectiveness and durability of active galvanic and passive barrier function of the ZRPs [5]. In these aspects, several ZRP compositions were studied revealing the influence of various size and shape of the pigments [6,7] as well as paint formulations [8]. Combination of the ICPs with sacrificial metallic grains is to retain galvanic function and reduce electrolytic conductivity of the ZRPs in the form of using stand-alone ICPs [9] or composited primers [10]. To amend inefficient mechanical blockage of conventional ZRPs [11] and to improve zinc-rich powder coatings [12], intrinsically conducting polymers (ICPs) have been successfully used as mild inhibitor agents to advance corrosion

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resistance of hybrid paints over ICP-free coatings. Further development was achieved by physical mixture of organic particles and inorganic pigments, but the idea to attain valuable improvement of galvanic protecting organic coatings relies on the formulation of hybrid paints containing highly dispersed particle supported ICPs along with the active anodic metallic pigments. Dispersity related problems of the ICPs are resolved in the course of coating preparation by following the approach of small carriers supported polymers [13]. These nano-size range particle supported ICPs allow to obtain highly dispersed composites [14–16] with greatly enhanced barrier properties [17,18]. The highly dispersed particles [15,14,19] feature increased conductivity and processibility [20] with improved corrosion protection ability [21]. Owing to the fact that zinc corrosion is effectively inhibited by PPy [22], carrier supported PPy is expected to be a favourite filler in zinc-rich hybrid paints. Although viable inhibition function of the PPy requires its partially oxidized form–doped state with immobile counter ion stabilisation [23], undoped ICPs are generally more favourable in paint applications [24] because of the compatibility with organic binders avoiding dispersability and binder compatibility related issues [25]. Although functionalized carriers can promote stable ICP doping, increased hydrophilicity of the materials remains to be addressed prior to successful anticorrosive paint adoption.

In these aspects, in this work PPy is used as nano-size alumina supported particles which are highly dispersed at submicron-scale in the primers so as to enhance electrical conductivity of the coatings and inhibit the corrosion of the zinc pigments. Although PPy deposited nano-size alumina was solely utilized in composite coatings to protect directly aluminium from corrosion [26], whereas the effects of various types of PPy modified alumina has been studied recently [27], the influence of altered ratio of the inhibitor particles and the sacrificial zinc pigments on the corrosion resistivity of particular hybrid formulations has not yet been disclosed. In an effort to achieve firm and durable corrosion prevention performance at the same time, this work is devoted to investigate various hybrid formulations in order to gain valuable improvement by certain zinc-rich compositions. Furthermore, the main scope is to find optimal balance between inhibition of sacrificial action of the zinc and galvanic function of the hybrid coatings by altered pigment/particle ratios.

2. Materials and methods

2.1. Synthesis of polypyrrole deposited alumina particles

Fumed alumina (Evonik Industries AG, Germany) was dispersed in aqueous ethanol (50 ml) by vigorous stirring for 1 h. Pyrrole (Aldrich) was dissolved at a concentration of 2×10^{-2} mol dm^{-3} and the suspension stirred for 2 h. Solutions (10 ml) of iron(III) nitrate (Fluka) and nitric acid (1 M) were added stepwise to the mixture stirred at 1800 rpm. The molar ratio of iron/pyrrole was set to 1.28 to gain acceptable polymerization rate, whereas pH of the dispersant was adjusted to 3 to moderate the rate of pyrrole polymerisation and deposition. After that low stirring rate (400 rpm) was applied for 6 h prior to the deposition of PPy. Then, the mixture was let stagnant for 16 h. PCAIPs were obtained by decantation, filtering off the precipitate and washing the solid neutral with water 12 times. Finally, the solid was dried and ground.

2.2. Preparation of paint coatings

Paint coatings were tested on standard, low-carbon cold-rolled steel panels (RS type CRS, complying with ASTM A1008.1010, A-109, and QQS-698 standards, roughness; 25–65 micro-inches) were used as received (Q-Lab Ltd., USA). No particular surface treatment was applied to steel specimens without introducing other methods raising the probability of decreasing repeatability of the corrosion tests.

The PCAIP sample was dispersed in the solution of epoxy dissolved by 80% xylene (Fluka), 10% 1-methoxy-2-propanol (Fluka) and 2-butanon (Aldrich) by 20 min milling. Suspension of the PCAIPs was mixed with component A–stabilised zinc-rich masterbatch (HZO Farbenzinkstaub, Norzinco GmbH) in epoxy (Epoxidharz CHS141, bisphenol-A epoxy resin, Prochema), which was diluted to set final concentration. Component B–poly(amido amine) cross-linking agent (Durepoxy H15VP, USNER) was added to the suspension stirred to homogenise, and diluted to get desired wet-concentration. Primer coatings were roll-blade casted in 90 μm wet thickness (35 ± 5 μm dry thickness) and let cure for a week at room temperature. Primers were top-coated with Macrynal SM 2810/75BAC hydroxyacrylic resin (CYTEC Industries Inc.) which was cured with aliphatic polyisocyanate resin; hexamethylene diisocyanate (Desmodur® N75MPA/X, Bayer MaterialScience LLC) dissolved in n-butyl acetate, xylene and isobutanol (2:2:1) in 120 μm wet thickness including hardened primer (80 ± 5 μm overall dry thickness), let cure for three weeks at 25 ± 3 °C. Scribes were made by a blade as X-cuts. Composition of the formulated paint coatings are summarised in Table 1.

2.3. Characterisation of polypyrrole deposited alumina particles

2.3.1. Elemental analysis

Elemental analysis was performed by a vario EL *III* micro and macro CHNOS elemental analyzer (Elementar Analysensysteme GmbH, Germany) with about 4 mg of the sample.

2.3.2. Transmission electron microscopy

The PCAIP was crushed under ethanol and deposited onto copper grids which were covered by carbon supporting films. Transmission electron microscopy (TEM) data were acquired with a FEI MORGAGNI 268(D) microscope (FEI Co., The Netherlands) operated at 100 kV, with tungsten filament (top-entry; point-resolution = 0.5 nm).

2.3.3. Rheology

Flow behaviour of suspensions and colloid sols is related to the interaction of dispersed particles. In addition, rheology control is sensitive to the extent (concentration and dispersity of solids)

Table 1
Zinc and the inhibitor particle contents of the cured primer and the epoxy resin of the paint coatings in weight percent (wt.%) and volume fraction (φ).

Coatings	PCAIP in the coating (wt.%)	PCAIP in the epoxy binder (wt.%)	PPy in the coating (φ)	PPy in the epoxy binder (φ)	Zinc (φ)
E	–	–	–	–	–
ZA	–	–	–	–	70 (26.8)
Z	–	–	–	–	90 (55.8)
H1	4.55	11.4	0.151 (3.28×10^{-3})	0.377 (4.02×10^{-3})	60 (18.3)
H2	3.67	9.3	0.121 (2.61×10^{-3})	0.308 (3.22×10^{-3})	60 (18.1)
H3	3.21	11.0	0.107 (2.81×10^{-3})	0.364 (3.89×10^{-3})	70 (25.8)
H4	1.75	9.1	0.060 (1.94×10^{-3})	0.301 (3.15×10^{-3})	80 (37.0)
H5	0.85	6.3	0.027 (1.07×10^{-3})	0.207 (2.14×10^{-3})	85 (45.0)