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Zinc-free varnishes and zinc-rich paints modified with ionic liquids

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ABSTRACT

The corrosion protection of a steel substrate using zinc-rich epoxy–alkyd paints (ZRPs) modified with either 1-hexyl-3-methylimidazolium hexafluorophosphate ($HMIMPF_6$) or 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMPyrrTFSI) has been investigated. Additionally, the influence of ionic liquids (ILs) on the corrosion process of uncoated steel and zinc as well as on electrical features of zinc-free varnishes has been evaluated. The pyrrolidinium IL significantly reduces the corrosion rates of steel and zinc but the ZRPs with $HMIMPF_6$ offer better cathodic protection of steel than unmodified ZRP and ZRPs with BMPyrrTFSI. The electrical conductivity of IL is not critical for the protective features of ZRP.

1. Introduction

Zinc-rich paints (ZRPs) are commonly used as primers or protective systems for steel substrates. Their corrosion inhibiting properties mainly depend on the electrical contact of anodic-active zinc particles thus grain shape [1,2], diameter [2–4] and pigment volume concentration (PVC) [1,5,6] of these additives are crucial parameters. In most cases ZRPs are compounded as 2 K liquid (epoxy or polyurethane-based [1,3,7–9]), 1 K liquid (epoxy ester [10], vinyl or orthosilicates-based [9,11]) and powder paints [12] with similar zinc volume content to its critical value (CPVC). Although PVC/CPVC ratio affects the quality of an electrical connection between zinc particles, coats with low binder content may be inhomogeneous and porous. Water (electrolyte) which migrates into the steel surface generally improves electrical contact of an anodic pigment and on the other hand, its presence allows the electrochemical process in Zn–Fe microcell. Zinc oxidation products (i.e. zinc oxide, zinc hydroxide, hydrozincite [13]) fill the coat pores and may also act as an electrical insulator in normal conditions. Nevertheless, in that situation a sealed zinc-rich coat exhibits higher barrier properties [14]. To improve the cathodic protection of a steel substrate by ZRPs, such coating compositions were modified using various solid components, e.g. Al dust, carbon black, polypyrrole, polyaniline and carbon nanotubes. These additives exhibit relatively high electroconductivity but upgraded corrosion protection of steel coated with the modified ZRP was noted only in several cases. Carbon black enhances the mentioned parameter (at content of 5 wt.% in a dry coat), however, technological problems of its incorporation into coating compositions occur also in the presence of the reduced amount of zinc powder [15]. Chen et al. revealed that the addition of aluminum dust does not significantly affect the resistance to the red rust formation of an air-sprayed paint based on an ethyl silicate binder [13]. Although polypyrrole [16] and polyaniline hydrochloride [17] inhibit the corrosion of zinc particles, the improved protective properties of ZRPs modified with the former additive were observed due to the upgraded epoxy binder resistance to the oxidative degradation. On the other hand, Armelin and co-workers [18] have reported that the emeraldine salt (ES) applied as a dispersion in xylene in the epoxy-based ZRP scavenges the chlorine anions preventing pitting corrosion of a coated steel substrate during its exposure in a marine environment. It has been also revealed that ES improves the protective features of zinc-free chlorinated rubber-based coats [19]. Interestingly, the ZRP with carbon nanotubes has been commercialized [20]. Generally, it should be expected that the properties of ZRP modified with the mentioned solid electroconducting additives depend on the additive particle size and their dissipation in a cured coat.

In this paper the protective properties of zinc-rich paints based on the epoxy–alkyd modified with ionic liquids (ILs) and applied onto a steel substrate have been presented and discussed. Two hydrophobic, relatively low-toxic commercial ILs, i.e. 1-hexyl-3-methylimidazolium hexafluorophosphate ($HMIMPF_6$) and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMPyrrTFSI) exhibiting miscibility with xylene and different electrical conductivity have been tested. Moreover, a direct influence of these ILs on binder features has been investigated by the analysis

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of zinc-free epoxy–alkyd-based varnishes. Although imidazolium-type ionic liquids act as efficient steel corrosion inhibitors in various electrolytes [21–24], the influence of 1,3-dialkylimidazolium hexafluorophosphates and 1,1-dialkylpyrrolidinium bis(trifluoromethylsulfonyl)imides on a steel substrate has not been revealed in literature yet.

2. Experimental

2.1. Materials

Solvent-borne epoxy–alkyd coating compositions were prepared using the following commercial components:

(1) WorléeDur D46, 60% solution in xylene of short oil epoxy ester based on conjugated drying fatty acids, epoxy resin content ca. 60 wt.%, oil content 40% (Worlée-Chemie GmbH, Germany).
(2) WorléeKyd P151, long oil alkyd resin based on special fatty acids, phthalic anhydride content 22 wt.%, oil content 64 wt.%, nonvolatile content >98 wt.% (Worlée-Chemie).
(3) HZO Zinc dust Superfine, zinc dust with $D_{50} = 3–4.5\ \mu m$ (Norzinco GmbH, Germany).
(4) 1-Hexyl-3-methylimidazolium hexafluorophosphate ($HMIMPF_6$) (IoLiTec GmbH, Germany).
(5) 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMPyrrTFSI) (IoLiTec).
(6) Octa-Soligen Calcium 7HS Neutral (OS-Ca), siccative based on the calcium salt of 2-ethylhexanoic acid (OMG Borchers GmbH, Germany).
(7) Octa-Soligen Cobalt 12 (OS-Co), the cobalt salt of 2-ethylhexanoic acid (OMG Borchers).
(8) Ascinin Anti Skin 0444 (A444); an anti-skinning agent, VOC-free synthetic proprietary product (OMG Borchers).
(9) A wetting/dispersing additive based on an unsaturated polycarboxylic acid polymer (BYK-P 104S, BYK-Chemie GmbH, Germany).
(10) A silicone defoamer (BYK-067A, BYK-Chemie).
(11) Xylene (90 wt.%) and butyl acetate (10 wt.%) mixture as a solvent (POCh S.A., Poland).

2.2. Zinc-free epoxy–alkyd varnish preparation

2.2.1. References varnish

WorléeDur D46 (90 wt. parts), WorléeKyd P151 (10 wt. parts), BYK 067A (0.2 wt. part/100 wt. parts of a binder), OS–Ca (0.1 wt. part of metal/100 wt. parts of a binder) as well as a solvent mixture were mixed using a laboratory dissolver with a heavy-duty dispersion impeller (VMA Getzmann GmbH, Germany) at 1000 rpm for 10 min. Then, OS–Co (0.03 wt. part of metal/100 wt. parts of a binder) and A444 (0.4 wt. part/100 wt. parts of paint) were incorporated and the system was mixed at 240 rpm for 10 min; the prepared varnish (EA–V) with 60% of solids was additionally homogenized at 400 rpm for 15 min (under nitrogen atmosphere) using a heavy-duty dispersion impeller.

2.2.2. Varnishes modified with ionic liquids

A zinc-free epoxy–alkyd varnish (EA–V) was mixed with an ionic liquid (0.92, 1.84 or 3.67 wt. parts/100 wt. part of solids) at 400 rpm for 15 min (under N_2 atmosphere) using a heavy-duty dispersion impeller. These ionic liquid doses correspond to 0.125, 0.25 and 0.5 wt. part of IL/100 wt. parts of zinc-rich paint solids (including zinc dust, a binder and auxiliary additives; see p. 2.3.). The physical properties of the applied ionic liquids are collected in Table 1 whereas the reference and a modified varnish recipe is specified in Table 2.

2.3. Zinc-rich epoxy–alkyd paint preparation

2.3.1. Reference paint

WorléeDur D46 (90 wt. parts), WorléeKyd P151 (10 wt. parts), BYK-P 104S (1.25 wt. part/100 wt. parts of zinc dust), BYK 067A (0.2 wt. part/100 wt. parts of a binder and filler content), OS–Ca (0.1 wt. part of metal/100 wt. parts of a binder/filler) as well as a solvent mixture were mixed using a laboratory dissolver with a heavy-duty dispersion impeller for 10 min (1000 rpm). Then, the zinc dust was added and the composition was homogenized at 2000 rpm for 1 h. Next, OS–Co (0.03 wt. part of metal/100 wt. parts of a binder/filler), A444 (0.4 wt. part/100 wt. parts of paint) and a solvent mixture were incorporated and the system was mixed at 240 rpm for 10 min; the prepared paint (EA–P) with 87% of solids was additionally homogenized for 20 min (2000 rpm) using a heavy-duty dispersion impeller.

2.3.2. Paints modified with ionic liquids

An unmodified zinc-rich epoxy–alkyd paint (EA–P) was mixed with an ionic liquid (0.125, 0.25 or 0.5 wt. part/100 wt. part of solids) at 2000 rpm for 20 min using a heavy-duty dispersion impeller. Compositions of the reference and modified paints (PVC/CPVC = 0.95) are presented in Table 2.

2.4. Sample preparation

The steel panels (ASTM A-1008) with a dimension of 76 × 152 mm (for adhesion and electrochemical analyses) and 102 × 152 mm (the salt spray test) were used as the substrates (Q-Panels, Q-Lab Europe, England). Pendulum hardness was determined using glass plates (100 × 100 mm).

Varnishes and paints were applied with a brush (according to the Polish Standard PN-C-81514:1979) and levelled with a film applicator (Unicoater 409, Erichsen GmbH, Germany) on a steel substrate and cured at room temperature for 14 days. Hardness and electrochemical impedance spectroscopic (EIS) measurements of zinc-free coats as well as the Tafel experiment for zinc-rich coats were carried out on one-layer samples made by using 100 μm and 150 μm (ZRPs) gap applicators, respectively. Two-layer samples for adhesion, immersion and salt spray tests were prepared by applying two layers of coating compositions (using 100 μm and 150 μm spiral applicators, consecutively) with 48 h coating intervals.

2.5. Test methods

The electrical conductivity of ionic liquids (δIL) was tested using the Elmetron CC-505 conductometer (Elmetron, Poland). The Fourier transform infrared spectroscopic (FT-IR) analysis of zinc-free cured coats was made by using the Nexus FT-IR spectroscope with attenuated total reflectance (ATR) accessories (Thermo Nicolet, USA). The pendulum hardness (Hp) (PN-EN ISO 1522:2008, König pendulum; three measurements for each sample) and adhesion to a steel substrate (Acc) (PN-EN ISO 2409:1999, a cross-cut method, three measurements) of cured coats were evaluated. Additionally, cross-cut adhesion tests after 500 h and 750 h of sample immersion in an aqueous NaCl solution (3.5 wt.%, air-saturated every 4 h) as well as after 1400 h of exposure in a salt spray chamber were performed.

Thickness of cured films was measured with the electronic film gauge Byko-test 8500 (BYK-Gardner GmbH, Germany) according to PN-EN ISO 2808. Digital images of a zinc-rich coat surface were made by using 3D Laser Scanning Microscope VK-9700 (Keyence, USA). Electrical resistance of cured varnishes containing ionic