



The combined role of inhibitive pigment and organo-modified silica particles on powder coatings: Mechanical and electrochemical investigation



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ABSTRACT

The addition of organo-modified silica particles (OSP) to powder coating containing zinc molybdenum phosphate pigment (ZMP) has been investigated. The OSP were directly incorporated at different concentrations (1, 2.5, 3.5 and 4.5 wt%) in a polyester powder monolayer coating with 10 wt% ZMP. The adhesion and anticorrosion properties were evaluated by means of adhesion studies and different electrochemical techniques: electrochemical impedance spectroscopy (EIS) and an accelerated cyclic electrochemical technique (ACET). The optimum quantity of OSP that gave maximum anticorrosive performance of the coating system was determined (1.0%), however two opposite effects of addition on the coatings led to a reduction of anticorrosive properties for higher contents. Finally, the electrochemical behaviour of the optimized combined system was compared to the effects achieved when both additives were separately added to powder coatings by means of an additional electrochemical test.

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1. Introduction

Corrosion protection by powder coatings is considered one of the most environmentally friendly mechanism to protect metallic substrates as they are essentially free of volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) [1]. Today powder coatings do not provide sufficient corrosion resistance for some applications yet, but some studies have demonstrated its superior performance in many aspects when compared to liquid coatings [2,3]. Initial primers or surface pretreatments prior to applying the coating are usually designed to facilitate adhesion to the substrate [4–6]. Although improved corrosion properties of these systems have been demonstrated, their two-step application involved an additional cost and entails environmental problems because in many cases chromium and other heavy metals are used [7]. Therefore many efforts in the field of metal protection are focused on the development of new materials to both simplify the protection system and be more environmentally friendly than traditional anticorrosion procedures.

Zinc molybdenum phosphate (ZMP) pigment has been proposed as an excellent alternative to toxic inhibitive pigments because of

equal or superior anticorrosive behaviour to chromates and better than zinc phosphate [8–10]. Certainly, zinc phosphate pigment has been strongly criticized by some coatings manufacturers for not providing the corrosion resistance required by standard specifications [11], so the development of new generations of zinc phosphate pigment with enhanced anticorrosive properties has become a necessity. ZMP pigment belongs to the second generation of zinc phosphates that are obtained by applying an organic surface treatment to the particles, designed to enhance the continuity between the inorganic pigment and the surrounding organic binder [12,13].

In another attempt to find environmentally safer alternatives to traditional methods in the field of corrosion control of metals, organosilane technology emerged in the last decades as a coupling agent substitute to replace chromate conversion coatings [14–17]. Nowadays continuous research on these advanced materials has led to new and different protection systems designs. Zhang et al. studied the direct incorporation of silane monomers into epoxy coatings [18]. Van Ooij group reported an improvement by incorporating silanes directly on a polyurethane resin system to obtain a 'superprimer' with outstanding adhesion and corrosion protection properties [19]. Further advances were also proposed by other authors consisting of the combination of montmorillonite nanoparticles or rare earths in silane sol-gel coating to enhance barrier properties and to achieve higher thickness and densification

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Table 1
Composition in weight (%) of the formulated coatings.

Nomenclature	Ref.	10 ZMP	2.5 OSP	1.0 Comb	2.5 Comb	3.5 Comb	4.5 Comb
Polyester resin	57.7	57.7	57.7	57.7	57.7	57.7	57.7
Crosslinking agent	3.3	3.3	3.3	3.3	3.3	3.3	3.3
TiO ₂	30.0	24.7	30.0	23.7	22.2	21.2	20.2
Barite	4.7	0.0	2.2	0.0	0.0	0.0	0.0
Flow ag.	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Levelling ag.	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Degassing ag.	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Pol. wax	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Tef. wax	0.2	0.2	0.2	0.2	0.2	0.2	0.2
ZMP pigment	0.0	10.0	0.0	10.0	10.0	10.0	10.0
OSP	0.0	0.0	2.5	1.0	2.5	3.5	4.5

[16,20–22]. Other recent studies report the development of hybrid coatings based on a silane functionalized epoxy resin to improve corrosion resistance [23].

In our recent investigation organo-modified silica particles with silanes were directly incorporated in different contents as an integral additive in a polyester powder monolayer coating to assess adhesion properties on galvanized steel without pretreatment [24]. The results determined the optimum concentration in 2.5 wt% due to the improvement in the adhesion and electrochemical properties of the coatings. In a further investigation, the optimum concentration of ZMP in the same polyester coatings applied on galvanized steel was also determined by means of electrochemical techniques [25]. The enhancement of anticorrosion properties when ZMP is added was attributed to both the improvement of barrier properties and the inhibitive action of the pigment.

In this study, the organo-modified silica particles (OSP) and zinc molybdenum phosphate pigment (ZMP) were simultaneously incorporated in a polyester system with the aim to combine the effects achieved when they were separately added to monolayer powder coatings in previous works. First, an optimum concentration of the combined system was determined by electrochemical, adhesion and salt fog spray tests. Finally, an additional electrochemical study was performed to investigate the possible existence of synergistic effect between the OSP and ZMP formulations.

2. Experimental

2.1. Materials

The coatings were developed from a saturated carboxylated polyester resin of low molecular weight (Reafree 8585 from Cray Valley Iberica, S.A.) to combine with a hydroxyalkylamide crosslinker (Primid-XL 552 from EMS-GRILTECH). Inorganic fillers and other additives used were titanium dioxide (Kronos 1171), barite (R-2 from Miber Minerales Roset), a flow agent (Additol from Cytec-Liquid Coatings Resins & Additives), a levelling agent (Cray-Vallac-PC from Cray-Valley Ibérica), a degassing agent (benzoin from DSM Special Products), a surface hardener (Licowax PE 520) and a teflon wax (Ceridust 9610F from Clariant).

ZMP pigment used in this work is based on zinc phosphate and zinc molybdate conditioned with an organic titanate in the surface (Nubiorox 106 supplied by Nubiola). The ZMP pigment was incorporated in a fixed content of 10% of the total formulation. The silane was a commercial additive consisting of trifunctional organosilane (alkyl-triethoxysilane) grafted to the surface of amorphous silica particles (reference ESQUIM DL-8302/7, supplied by Esquim S.A., Barcelona). Different concentrations of the additive (OSP) were incorporated into the formulations replacing the inorganic filler (TiO₂) except in the 2.5 OSP formulation that replaces the barite.

Table 1 summarizes the compositions of the samples studied in this work.

2.2. Substrate/sample preparation

Samples were premixed and hand-shacked before extruding in a single screw extruder (Haake Rheomex 254). The extrusion temperature was set to 100 °C, the residence time was approximately 1 min and the torque generated was 20 Nm. After that, the materials were ground in a Moulinex Mill MX843 and sieved through a mesh size of 140 μm. The five different powder coatings were deposited over galvanized steel substrates, previously degreased with acetone, by means of an electrostatic gun. All the coated samples were cured at 180 °C for 15 min and the thicknesses obtained were 90 ± 10 μm.

2.3. Testing methods and equipment

2.3.1. Scanning electron microscopy (SEM)

The morphology of the coatings was observed by scanning electron microscopy (LEO 440i SEM) with a digital image acquisition. Samples studied were obtained from coatings detached from the substrates after cryofracturing. The back-scattered and secondary electron images were complemented by appropriate chemical information from energy dispersive X-ray analysis (EDS) acquired as point and/or line scans.

2.3.2. Mechanical tests

2.3.2.1. Impact resistance test. Impact test was performed in accordance to ISO 6272-2:2002. The operation principle of the impact tester is a 1 kg dart mass that drops down from different heights up to 1 m and impacts the back of the painted panel to result in its rapid deformation. Coating resistance to impact may be determined from observing whether the film cracked or peeled off.

2.3.2.2. Cross-cut test. Paint adhesion was investigated in accordance to ISO 2409:2007, using a cutter with six blades that makes 2 mm square lattice cuts wide on the coating film. The cuts were made through the coating film with steady motion using just sufficient pressure on the knife. The samples were visually evaluated to detect any delamination of the film. The classification of the delaminated film was based on the criteria and standard stipulated in the ISO 2409:2007.

2.3.2.3. Adhesion test. Adhesion test was performed in accordance to ISO 4587:2003. Specimen preparation procedure for adhesion test consists on the deposition of the coatings with different adhesion promoter contents between two rectangular and degreased steel substrates, as was prepared in previous works [26], and cured at 180 °C for 30 min. After the curing process, the samples were tested using an Instron Universal Test Machine 4469 H 1907 with a load cell of 50 kN at a crosshead speed of 1 mm/min. Data of load and

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