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Anticorrosive 2K polyurethane paints based on nano- and microphosphates with high dispersing additive content

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ABSTRACT

Two-component solvent-borne polyurethane paints containing mica, quartz, TiO_2, wollastonite, talc as well as either nanosized aluminum phosphate or microsized aluminum-zinc phosphate as anticorrosive filler have been tested. Three paints with various PVC and CPVC values had been prepared and applied onto steel substrate and cured at room temperature. An influence of commercial dispersing additive dose as well as a type and content of phosphate filler on features of tested paints and coatings has been investigated. However, the incorporation of nanosized aluminum phosphate into coating compositions increases their viscosity the cured paints exhibit higher adhesion to a steel substrates in comparison with coats based on microsized aluminum-zinc phosphate (both samples characterized with the same PVC value). Moreover, higher dose of dispersing additive causes higher value of the former parameter and either improves (in case of coats with nanofiller) or reduces adhesion (coats with microfiller). The results of corrosion tests in a salts spray chamber showed that paint system containing 9.8 wt.% of nanosized aluminum phosphate and 7.5 wt. parts of dispersing additive (per 100 wt. parts of all fillers/pigment content in coating compositions) had better protective properties than polyurethane coats containing 12.2 or 15.6 wt.% of commercial microsized aluminum-zinc phosphate and various auxiliary dispersing additive content.

1. Introduction

Organic binder and fillers/pigments mixture comprise the main components of protective organic coating compositions. However, area of paints application usually depends on a type and dose of these ingredients quality of the paints is directly affected by auxiliary additives. They facilitate film application (e.g. rheology modifiers, anti-sagging additives), enhance film appearance (defoamers, UV absorbers, leveling additives, dispersing additives) and facilitate paint manufacturing processes. In most cases special additives upgrade mechanical, chemical and barrier features of cured coats (adhesion promoters, substrate wetting and dispersing additives) [1–3]. Dispersing substances markedly influence on decorative properties of pigmented paints (mainly improve their hiding power and gloss) as well as protective efficiency of high filled coating compositions. Commercial dispersing substances are commonly intended for microsized reinforcing and anticorrosive fillers and there are lots of clues regarding selection of dissipating additives (involving both their type and typical content in specific coating composition). In case of nanofillers, e.g. organophilized montmorillonites, carbon nanotubes and metal oxides their small quantities (<5 wt. parts) are mostly incorporated into conventional coating compositions using by simple or sophisticated dispergation methods with no extra auxiliary substances [4–7]. On the other hand, large amounts of nanosized inorganic fillers (with the exception of TiO_2 [8,9] and inactive nanofillers/nanoextenders such as barium sulfate [9], calcium carbonate [10]) have not been used as a main components of paints thus useful technical and scientific information about selection and efficiency of dispersing additives in these systems is not available.

In this work the nanosized aluminum phosphate filler has been tested as an anticorrosive component of 2 K polyurethane paint. However, microsized aluminum phosphate exhibits relatively high anticorrosive efficiency with various coating binders [11–13] the nanoparticles of that pigment have been so far commercially used as a rutile-type titanium dioxide substitute in exterior high quality decorative waterborne top-coats [14]. Results of mechanical and anticorrosive laboratory tests of polyurethane paint containing nanosized aluminum phosphate, prepared via reaction of aluminum sulfate and diammonium phosphate in aqueous medium have been published lately [15]. That coating system based on relatively high dose of selected commercial dispersing additives

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(i.e. 2.5 wt. parts/100 wt. parts of pigment/fillers) had exhibited in general lower protective features than paints based on microsized aluminum-zinc phosphate filler. This paper concerns coating compositions prepared using tripled amount of dispersing additive in comparison with previously described paints [15]. Pigment volume concentration value (PVC = 18.3) as well as the Λ parameter value (PVC/critical pigment volume concentration CPVC = 0.55) for prepared coating systems have been chosen on the basis of the literature data [16].

2. Experimental

2.1. Commercial materials

Two-component solvent-borne polyurethane paints were based on the following components:

- WorléeCryl A2120, 50% solution of hydroxyacrylic resin in butyl acetate, viscosity ca. 900 mPa s at 23 °C, hydroxyl value 66 mg KOH/g (on solids) (Worlée-Chemie GmbH, Germany);
- Tolonate IDT 70B, 70% solution of isophorone diisocyanate derivative in butyl acetate, viscosity ca. 600 mPa s at 25 °C, NCO content 12.3 wt.% (Perstorp AB, Sweden);
- aluminum-zinc phosphate (FAC) (Złoty Stok Farby Sp. z o.o., Poland);
- mica/quartz mixture, specific gravity 2.75 g/cm^3, oil absorption 35 g/100 g (Aspolit F40, Aspanger Bergbau & Mineralwerke GmbH, Austria);
- titanium dioxide (TiO_2), specific gravity 4.1 g/cm^3, oil absorption 21 g/100 g (Tytanpol R001, Z.Ch. Police S.A., Poland);
- alkylsilane treated wollastonite, specific gravity 2.85 g/cm^3, oil absorption 40 g/100 g (Tremin 939-300 FST, Quarzwerke GmbH, Germany);
- talc, specific gravity 2.75 g/cm^3, oil absorption 49 g/100 g (Finntalc M03-SQ, Mondo Minerals OY, Finland);
- butyl acetate (30 wt.%) and xylene (70 wt.%) mixture as a solvent (POCh S.A., Poland);
- dispersing additive based on unsaturated polycarboxylic acid polymer (7.5 wt. parts/100 wt. parts of total pigment/fillers content, BYK-P 104S, BYK-Chemie GmbH, Germany);
- silicone defoamer (0.1 wt. part/100 wt. parts of paint, BYK-067A, BYK-Chemie GmbH).

2.2. Phosphate fillers preparation and characterization

Nanosized aluminum phosphate (nAP) was prepared via a reaction of aluminum sulfate (≥99%, ChemPur, Poland) and diammonium phosphate (≥99%, POCh, Poland) (molar ratio Al:PO_4^{3-} 1:1) in an aqueous solution (pH 4.1) at 20 °C. Preparation method, physical and chemical properties of the mentioned aluminum phosphate (as well as features of commercial aluminum-zinc phosphate) have been previously analysed by authors in detail [15] and are presented in Table 1. Particles (or their agglomerates) size distribution of either aluminum phosphate or aluminum-zinc phosphate dispersed by sonication (25 min, UPS400S, Hielscher Ultrasonics GmbH, Germany) in xylene/butyl acetate (70/30 m/m) mixture containing BYK-P 104S in amount 2.5 or 7.5 wt. parts/100 wt. parts of phosphate filler has been analyzed using a light scattering technique (Zetasizer Nano, Malvern, UK). Additionally, deposits of phosphate fillers in tested suspensions have been separated, washed with solvent mixture, dried and weighted.

2.3. Paint preparation

Moisture-free phosphate filler (nAP or FAC) and TiO_2 were preliminary dispersed (0.5 h, 25 °C) in solvents containing both a dispersing agent and defoamer, using a laboratory dissolver DIAX 900 (Heidolph, Germany) at ca. 10,000 rpm. Next the slurry was dispersed for 1 h with a part of WorléeCryl A2120, mica/quartz mixture, talc as well as wollastonite in a pearl-mill (Klaxon, UK) filled with glass pearls ϕ 2.3–2.6 mm. Then, the paste was mixed (for 1 h) with the rest of the hydroxyacrylic component using a laboratory dissolver with a heavy-duty dispersion impeller (VMA Getzmann GmbH, Germany) at 1200 rpm. The prepared paint component was filtered (190 μm) and mixed with a diisocyanate hardener using a laboratory mixer. Paints components as well as PVC and CPVC values are specified in Table 2. Coating composition containing nanosized aluminum phosphate is abbreviated to PU/nAP while these filled with microsized aluminum-zinc phosphate are described as PU/FAC.

2.4. Sample preparation

The steel plates were ground with the P-240 type abrasive paper and degreased with acetone and toluene. The substrate panels with a dimension of 80 mm × 100 mm (for adhesion) and 100 mm × 100 mm (for electrochemical impedance spectroscopy analysis) were used in the experiments. Pendulum hardness was determined using glass plates (100 mm × 100 mm). Samples for a salt spray test were prepared using steel plates (Q-Panels, 152 mm × 102 mm) supplied by Q-Lab Europe (England).

Paints were applied with a brush (according to the Polish Standard PN-C-81514:1979) and leveled with a spiral film applicator (150 μm, Unicoater 409, Erichsen GmbH, Germany) on the steel substrate and cured at room temperature for 14 days. The two-layer samples for electrochemical impedance spectroscopy (EIS) tests as well as salt spray tests were prepared by applying two layers of coating compositions with 24 h painting intervals.

2.5. Characterization of coating compositions and cured paints

High-share viscosity tests (I.C.I. cone-plate system, Research Equipment Ltd., England) were performed on ready-to-use liquid coating compositions. The pendulum hardness (PN-EN ISO 1522:2008, König pendulum; four measurements for each sample) and pull-off adhesion tests (PN-EN ISO 4624:2004, PHO-4 hydraulic apparatus, Dozafil, Poland; ten measurements for each composition) were evaluated on the cured paints. Thickness of cured films was measured with an electronic film gauge Byko-test 8500 (BYK-Gardner GmbH, Germany) according to PN-EN ISO 2808. Digital images of cross-section micrograph of cured polyurethane coats were made using 3D Laser Scanning Microscope VK-9700 (Keyence, USA). EIS tests were carried out with coated panels (two-layer coats with 180–229 μm thickness) after 3, 24 and 48 days of their exposure to an aqueous NaCl solution (3.5 wt.%). After every three days of immersion in the NaCl solution, the samples were dried at room temperature for 1 day and then put again into a fresh dose of a NaCl solution. EIS measurements were carried out by using three coated samples for each tested composition. A three-electrode glass cell (with a 16.6 cm^2 surface sample area equipped with a graphite counter electrode and a saturated calomel reference electrode) were used inside the Faraday cage. The impedance data (at frequency 0.01–30,000 Hz, 100 mV amplitude of sinusoidal voltage) were collected by using EIS300 software with FAS2 femtostat (Gamry, USA) and then analyzed by using Gamry Echem Analyst software in relation to the electric circuit model presented in Fig. 1 (Ru – uncompensated solution resistance, Rp – pore resistance, Cc – coating capacitance) [17]. Pore resistance parameter (mainly