



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, TiO₂, 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.

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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 TiO₂ [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 micro-sized 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 Δ 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/cm³, oil absorption 35 g/100 g (Aspolit F40, Aspanger Bergbau & Mineralwerke GmbH, Austria);
- titanium dioxide (TiO₂), specific gravity 4.1 g/cm³, oil absorption 21 g/100 g (Tytanpol R001, Z.Ch. Police S.A., Poland);
- alkylsilane treated wollastonite, specific gravity 2.85 g/cm³, oil absorption 40 g/100 g (Tremin 939-300 FST, Quarzwerke GmbH, Germany);
- talc, specific gravity 2.75 g/cm³, 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 ($\geq 99\%$, ChemPur, Poland) and diammonium phosphate ($\geq 99\%$, 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 TiO₂ 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 μ m) 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 micro-sized 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 \times 100 mm (for adhesion) and 100 mm \times 100 mm (for electrochemical impedance spectroscopy analysis) were used in the experiments. Pendulum hardness was determined using glass plates (100 mm \times 100 mm). Samples for a salt spray test were prepared using steel plates (Q-Panels, 152 mm \times 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 μ m, 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 μ m 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 cm² 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

Table 1
Physical and chemical properties of nanosized aluminum phosphate and microsized aluminum-zinc phosphate [15].

Anticorrosive filler	Aluminum phosphate (nAP)	Aluminum-zinc phosphate (FAC)	Analysis methods
Specific density (g/cm ³)	2.59	3.30 ^a	Pycnometry
Average particle size (μm)	0.255	≤63 ^a	Light scattering technique
Oil absorption (g/100 g)	151	35 ¹	Linseed oil absorption
Surface area (m ² /g)	81.9	5.8	Brunauer–Emmett–Teller test
Al content (wt.%)	19.2	4.2	Complexometric (using EDTA)
Zn content (wt.%)	0	32.5	Colorimetric (vanadium-molybdenum test)

^a Manufacturer information.

Table 2
Coating composition.

Coating system acronym		PU/nAP	PU/FAC-1	PU/FAC-2
Pigment volume content (vol.%)	Aluminum phosphate	30	–	–
	Aluminum-zinc phosphate	–	30	30
	Mica/quartz mixture	35		
	TiO ₂	20		
	Wollastonite	10		
	Talc	5		
Phosphate content (wt.%)		9.8	15.6	12.2
	PVC	18.3	25.9	18.3
	CPVC	33.3	47.1	47.1
	Δ	0.55	0.55	0.39

connected with electrolyte absorption in coats) and coating capacitance (usually depended on water absorption in tested sample) were calculated in respect to coat thickness and presented in the paper as a relative Rp (i.e. Rpr) and relative Cc (Ccr) with deviation.

The salt spray test was carried out according to PN-EN ISO 9227:2007 in CorrosionBox 400 (Co.Fo.Me.Gra., Italy) using an aqueous NaCl solution (concentration of 50 ± 5 g/l) sprayed with compressed oil-free air (100 kPa). The back side and edges of steel panels with x-cut coats (coats thickness 185–221 μm, x-cut according to EN ISO 17872:2007) were protected with a special pressure adhesive tape (TESA Tape, USA) and mounted at an angle of 20° vertically. The temperature in a spray cabinet was maintained at 35 °C.

3. Results and discussion

The viscosity values of liquid coating composition based on nanosized aluminum phosphate and compositions with commercial aluminum-zinc phosphate are presented in Fig. 2. Paint filled with nAP filler exhibits significantly higher viscosity (i.e. 2.9 Pa s) than PU/FAC-2 (2.5 Pa s) and PU/FAC-1 (2.3 Pa s) paints. It can be seen that mentioned viscosity values are inversely proportional to the phosphate filler weight content in the coating composition (PU/nAP composition contains the lowest while PU/FAC-1 the highest amount of phosphate). Nevertheless, taking into consideration the PVC values of coating compositions, the PU/nAP paint reaches much higher viscosity than PU/FAC-2 (both systems with PVC = 18.3, Table 2). Presented relationship has also been found in case of identical polyurethane paints (based on either nAP or FAC filler) containing lower amount of dispersing additive (i.e. 2.5 wt. parts) but viscosity values for those coating compositions were markedly lower; paints filled with nAP (PVC = 18.3, PU/nAP*) reached 2.1 Pa s while compositions with FAC exhibited 1.2 Pa s

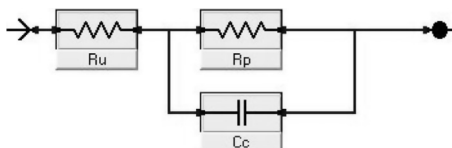


Fig. 1. Electric circuit model of coats utilized to EIS data analysis.

(PVC = 25.9, PU/FAC-1*) and 1.8 Pa s (PVC = 18.3, PU/FAC-2*) [15]. It should be noted that viscosities of PU/nAP and PU/FAC-2 (i.e. paints containing 7.5 wt. parts of dispersing additive) are about 40% higher than values observed for PU/nAP* and PU/FAC-2*, respectively. It might confirm that larger dose of commercial auxiliary substance really causes better dispergation efficiency of tested anticorrosive filler (and/or the other incorporated pigments and fillers) in paint compositions. Nevertheless, the results of particle size analysis of either nAP or FAC suspension in solvent mixture (containing 2.5 or 7.5 wt. parts of dispersing additive/100 wt. parts of filler; Figs. 3 and 4, respectively) as well as analysis of phosphate filler deposits amount (Table 3) show that higher additive dose affects better dissipation of higher amount of nAP nanoparticles or better dissipation of finite small amount of microsized aluminum-zinc phosphate (i.e. fine-grained fraction of FAC). It can be seen that aluminum phosphate dispersion with 7.5 wt. parts of dispersing additive (nAP-7.5) contained lower quantity of filler deposit (26 wt.% of incorporated phosphate filler) than system based on lower dose of that substance (nAP-2.5, 46 wt.%). Moreover, the latter system contained well-dispersed particles of phosphate filler and a small amount of dissipated agglomerates (Fig. 3, nAP-2.5) while the nAP-7.5 compositions comprised quite a number of agglomerates. In case of both dispersions containing aluminum-zinc phosphate the filler deposit amounts are similar (91 wt.% for

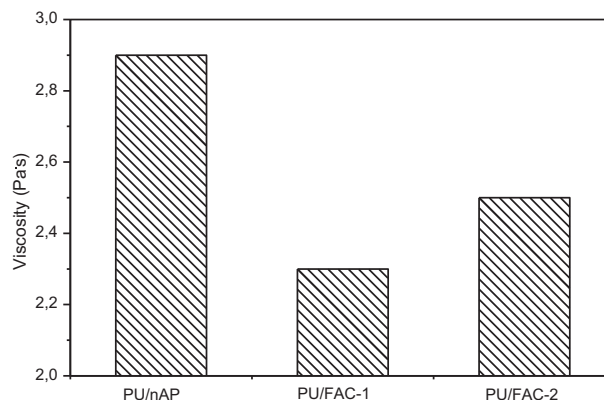


Fig. 2. Viscosity of liquid polyurethane paints.

Table 3
Characteristic of sonicated phosphate filler dispersions.

Phosphate filler acronym	Dispersion acronym	Dispersing additive content ^a (wt. parts)	Particle size distribution (nm)		Filler deposit amount (wt.%)
			Peak 1	Peak 2	
nAP	nAP-2.5	2.5	295	1106	46
	nAP-7.5	7.5	1484	295	26
FAC	FAC-2.5	2.5	190	825	91
	FAC-7.5	7.5	164	295	87

^a Weight parts/100 weight parts of phosphate filler.

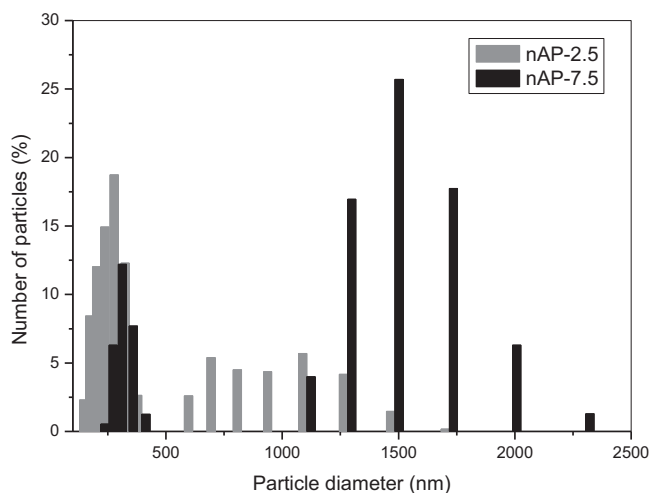


Fig. 3. Size distribution by number of aluminum phosphate (nAP) particle dispersed with various amount of dispersing additive.

FAC-2.5 and 87 for FAC-7.5, respectively) and phosphate agglomerates only appeared in FAC-2.5 system (Fig. 4). It confirms that higher dispersing agent dose than 2.5 wt. parts (per 100 wt. parts of pigment) causes significantly better dispersion of nanosized aluminum phosphate in non-polar solvent mixture (thus in tested polyurethane liquid coating composition). Graphical qualitative presentation of discussed effect of auxiliary additive content on phosphate fillers dispersion is visualized in Fig. 5.

Higher content of dispersing additive in coating composition remarkably influences on cured paint adhesion to a steel substrate. Tested coat based on nanosized aluminum phosphate

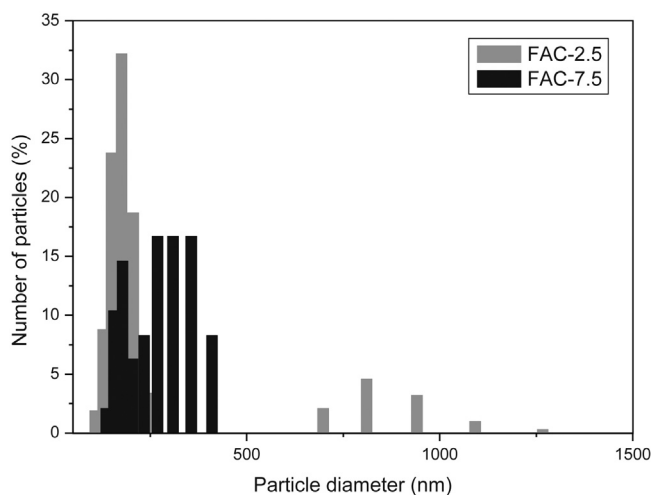


Fig. 4. Size distribution by number of aluminum-zinc phosphate (FAC) particle dispersed with various amount of dispersing additive.

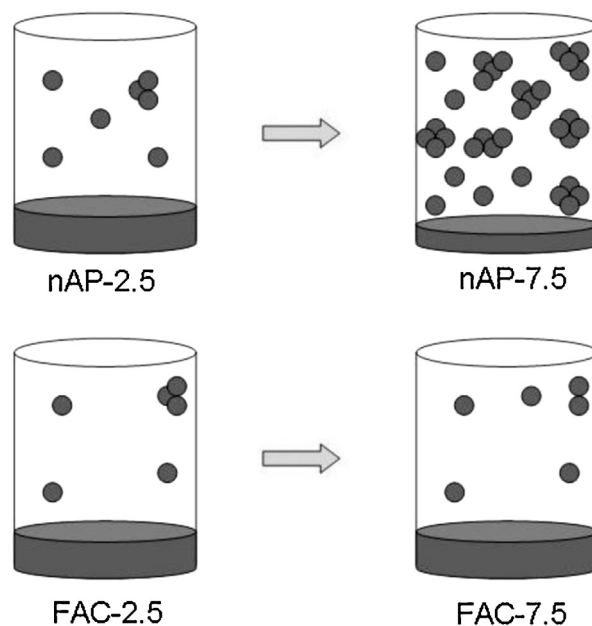


Fig. 5. Dispersion models of aluminum phosphate and aluminum-zinc phosphate suspensions with various amount of dispersing additive.

(PU/nAP) reached higher value of that parameter (i.e. 1.46 MPa, Fig. 6) in comparison with composition containing a lower dose of aforementioned additive (1.0 MPa for PU/nAP*) while adhesion of PU/FAC-2 was reduced from 2.5 MPa (PU/FAC-2* [15]) to 0.98 MPa. Probably better pull-off adhesion of nanofiller based coats (containing higher amount of auxiliary dispersing additive) to a steel is directly caused by enhanced dispersion of nanofiller (and other fillers/pigments) in polymer matrix; in case of PU/FAC-2 the detrimental effect of unnecessary additive excess has been revealed. Adhesion values of PU/FAC-1 and PU/FAC-1* to a steel substrate were similar and reached 1.9 MPa and 1.8 MPa [15], respectively. It

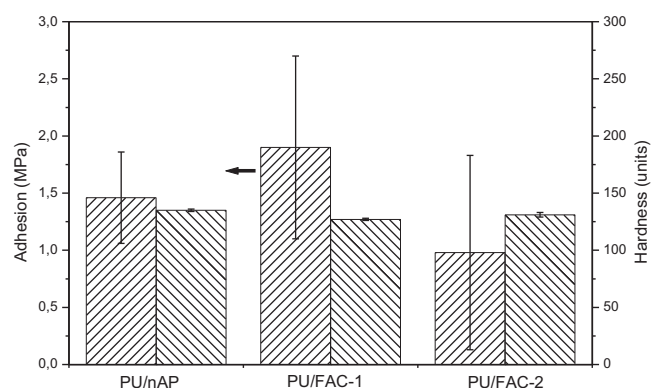


Fig. 6. Pull-off adhesion and hardness values of cured polyurethane coats.

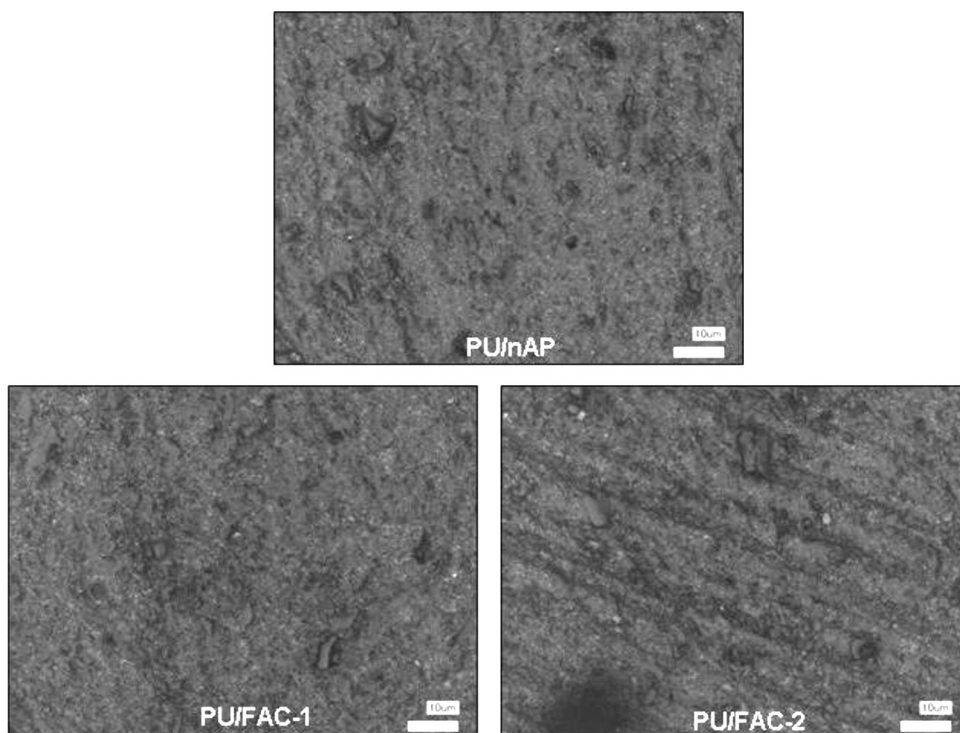


Fig. 7. LSM images of cross-section micrographs of cured polyurethane coats.

can be seen that samples based on aluminum phosphate nanofiller (PU/nAP) exhibited lower adhesion to a steel substrate than samples with highest content of aluminum-zinc phosphate microfiller (PU/FAC-1) but the former coats significantly better adhere to steel than PU/FAC-2. Generally, coats with the same volume content of polymeric binder, i.e. PU/nAP and PU/FAC-2 (PVC = 18.3) were characterized by adhesive failure from the steel substrate (separation between coat and steel substrate) while in case of PU/FAC-1 (PVC = 25.9) the adhesive/cohesive-type failures have been noted. Although PU/FAC-1 contains the lowest amount (by volume) of binder the failures observed during adhesion test had not been affected by limited dissipation of pigments/fillers particles in PU matrix. Agglomerates of phosphates as well as the other grainy components have not been observed in a cross-section micrograph of the paint layers (Fig. 7); used pigments and fillers had been uniformly dispersed in all prepared polyurethane compositions. Pendulum hardness of cured paints is also presented in Fig. 6. Coats filled with phosphate nanofiller reached significantly higher value of that parameter (i.e. 135 units) than both compositions containing microsized aluminum-zinc phosphate (127 units noted for PU/FAC-1 and 131 units for PU/FAC-2). Addition of dispersing substance in a lower amount has not significantly affected hardness values, i.e. 138 units for PU/nAP*, 128 units for PU/FAC-1* and 131 units for PU/FAC-2* were found out [15].

The delamination range around the scribe and blistering observations of cured PU paints (exposed in a salt spray cabinet for 500 h, 750 h and 1000 h) are presented in Table 4. Moreover, the digital photographs of coated panels tested for 1000 h (and additionally photographs of steel bases after coats removal) are shown in Fig. 8. An average width of delamination area around the scribe noted for PU/nAP coats was 4.1 mm (after 500 h) and increased to 5.5 mm (750 h) and 6 mm (1000 h of exposition). Distinctly worse results were observed for PU coats filled with microsized aluminum-zinc phosphate. However, samples with FAC exhibited admissible loosening of their adhesion around the scribe after testing for 500 h (5.9 mm for PU/FAC-1, 5.5 mm for PU/FAC-2) and 750 h (6.5 mm and 9.6 mm, respectively) these coats reached

unacceptable delamination value (>20 mm) after 1000 h of their exposure in a corrosion cabinet. Exfoliation of the coat around the scribe observed for samples based on commercial aluminum-zinc phosphate correlates with adhesion values of these samples before salt spray test (Fig. 6). Cured PU/FAC-1 paint better adheres to a steel panels than PU/FAC-2 therefore the former coating system exhibited lower tendency to delamination and blistering during anticorrosive test [3(S2), Table 4]. Nevertheless, polyurethane coats filled with nanosized aluminum phosphate reached a significantly higher blistering resistance [2(S2) after 1000 h] than samples with FAC filler. Generally, higher anticorrosive properties were observed for PU coats characterized by the same Δ value (i.e. 0.55); in case of samples protected with either PU/nAP or PU/FAC-1 coats much less corrosion products have been found on the base surface of steel panels, as well (Fig. 8). Taking into consideration the dispersing additive content in coating compositions the PU/nAP coats exhibited significantly lower delamination around the scribe as well as lower blistering in comparison with PU/nAP* samples [>20 mm and 3(S4) after 1000 h of exposure in a salt spray cabinet]. On the other hand higher dose of auxiliary additive reduces anticorrosive features of coats based on commercial aluminum-zinc phosphate (PVC = 18.3) from 11.1 mm and 2(S4) (PU/FAC-2* [15]) to much more than 20 mm of delamination around the scribe after salt spray test.

The salt spray chamber test results slightly correlate with EIS data obtained using an electric circuit model presented in Fig. 1. Although samples containing nanosized aluminum phosphate had a lower relative pore resistance values after 3 and 24 days of immersion (i.e. 4.06 M Ω /μm and 25.9 k Ω /μm, Fig. 9) in relation to samples with aluminum-zinc phosphate these coats with nAP exhibited a higher Rpr at the end of the test (686 k Ω /μm) than PU/FAC-1. In case of samples with FAC the analyzed parameter has decreased during whole test and reached 18.4 k Ω /μm (PU/FAC-1) and 20.0 M Ω /μm (PU/FAC-2) after immersion for 48 days. The Rpr value increment observed after that period for PU/nAP is clearly revealed in Bode plots (Fig. 10(A) and (B)) and was probably affected by a high content of dispersing additive in coats (i.e. 7.5 wt. parts/100 wt. parts of pigment/fillers). That component

Table 4
Delamination value and blistering degrees of painted steel panels exposed in a salt spray chamber.

Salt spray test duration (h)	Delamination around the scribe (mm) ^a			Blistering outside of the scribe ^b		
	PU/nAP	PU/FAC-1	PU/FAC-2	PU/nAP	PU/FAC-1	PU/FAC-2
500	4.1	5.9	5.5	0 (0)	0 (0)	0 (0)
750	5.5	6.5	9.6	0 (0)	0 (0)	0 (0)
1000	6.0	>20	>20	2 (S2)	3 (S2)	–

^a According to EN ISO 4628-8.

^b Described as “frequency(size)” of blisters according to EN ISO 4628-2.

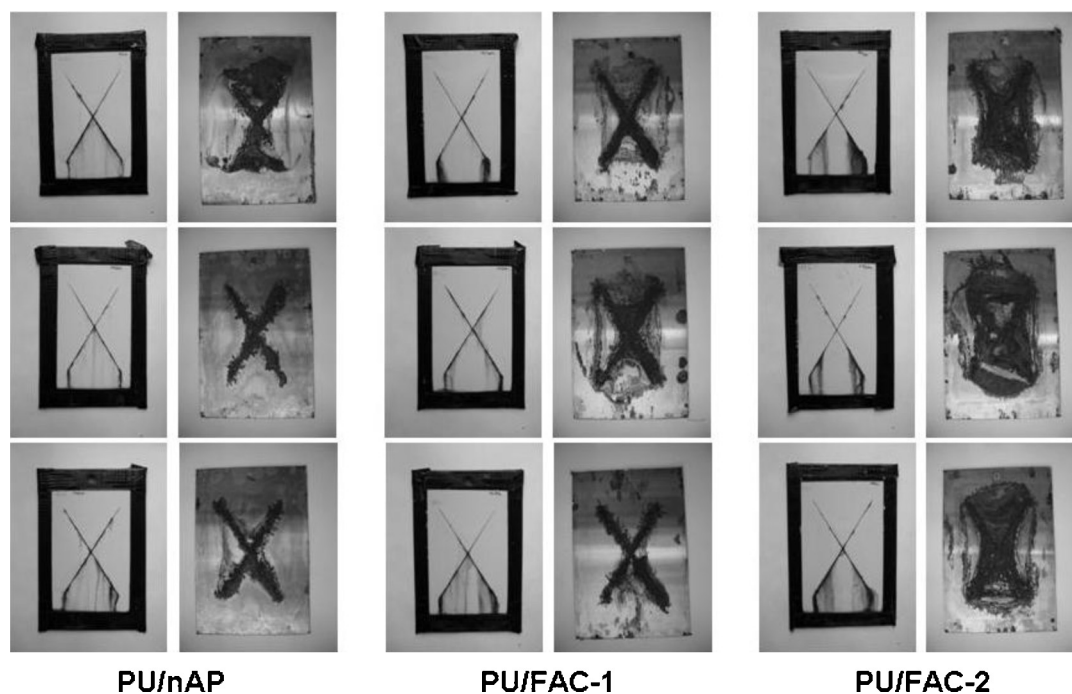


Fig. 8. Coated steel samples (left) and steel samples with removed coats (right) after exposure for 1000 h in a salt spray chamber.

is based on unsaturated polycarboxylic acid polymer therefore it could influence on electric features of analyzed samples. Relative pore resistances of similar polyurethane coats based on either nAP or FAC filler and 2.5 wt. parts of aforementioned additive were relatively higher ($R_{pr} > 41 \text{ M}\Omega/\mu\text{m}$ after 48 days) as well as more stable during the immersion test [15]. However, such a phenomenal increment of R_{pr} value has not been evidenced in previous research

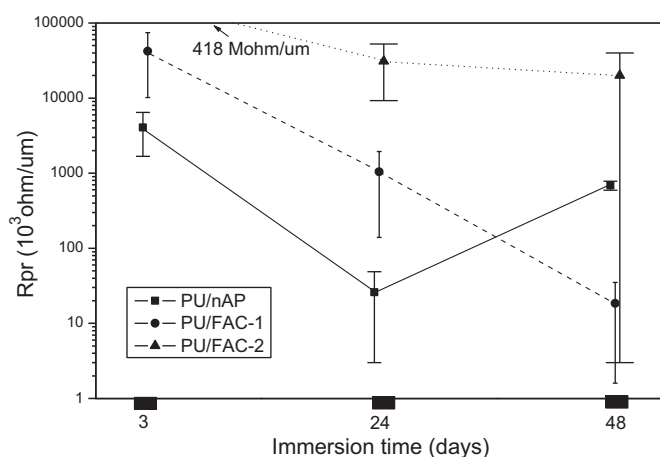


Fig. 9. Relative pore resistance (R_{pr}) variation of coats during the immersion in an aqueous NaCl solution.

the mentioned PU/nAP* coats with nanosized aluminum phosphate (incorporated in the same proportion as in case of PU/nAP) exhibited higher delamination value around the scribe and far lower blistering resistance during exposure in a salt spray cabinet. On the other hand, these parameters have been markedly deteriorated after addition of tripled amount of the polycationic dispersing additive into coating compositions containing 12.2 wt.% of microsized aluminum-zinc phosphate (PU/FAC-2, Table 4).

The relative coat capacitance values calculated for tested coats are presented in Fig. 11. The Ccr of samples with nanosized aluminum phosphate rose from $4.9 \text{ pF}/\mu\text{m}$ (after 3 days of the test) to $7.4 \text{ pF}/\mu\text{m}$ (48 days) while that parameter value for PU/FAC-2 was varying (during the analyzed period) in a narrow range between $5.4 \text{ pF}/\mu\text{m}$ and $5.3 \text{ pF}/\mu\text{m}$. Coats with larger content of aluminum-zinc phosphate exhibited Ccr value between PU/nAP and PU/FAC-2 and reached $6.2 \text{ pF}/\mu\text{m}$ after 48 days of the immersion test. Taking into consideration the recipe of tested coats the highest and the lowest values of Ccr have been observed for compositions characterized with $\text{PVC} = 18.3$ (PU/nAP and PU/FAC-2, respectively). The former composition was based on phosphate filler with extremely high surface area ($S_{\text{BET}} = 81.9 \text{ m}^2/\text{g}$) while the latter system contained lower amount of FAC ($S_{\text{BET}} = 5.8 \text{ m}^2/\text{g}$) in comparison with PU/FAC-1. So, as can be seen the coat capacitances of tested polyurethane coats directly depends on value of interfacial area between polymeric matrix and dispersed filler. Water absorbed from the immersion medium has acted in that place as capacitor spacer therefore the higher Ccr for coats filled with nanofiller was observed.

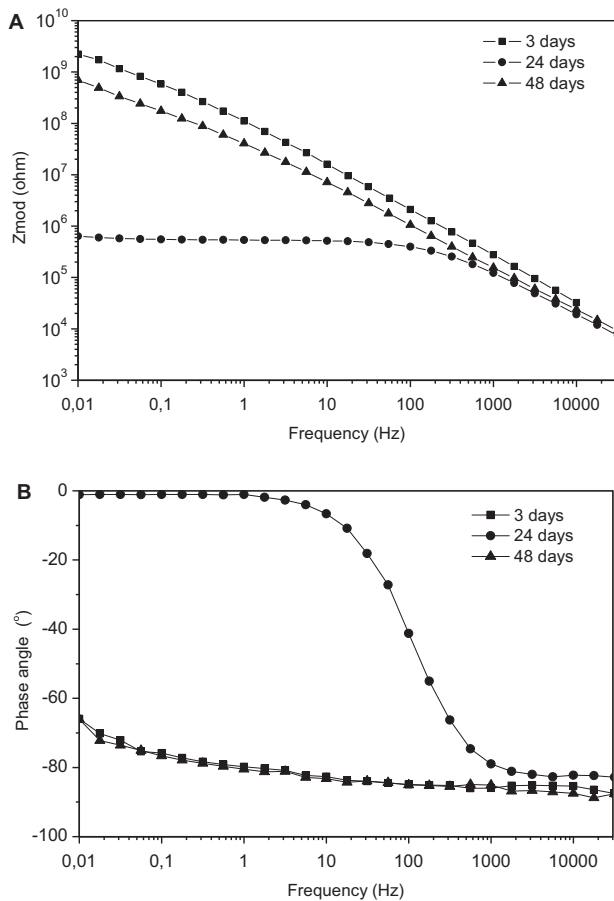


Fig. 10. Bode plots for PU/nAP coat after 3, 24 and 48 days of immersion in an aqueous NaCl solution: (A) impedance spectra and (B) phase angle.

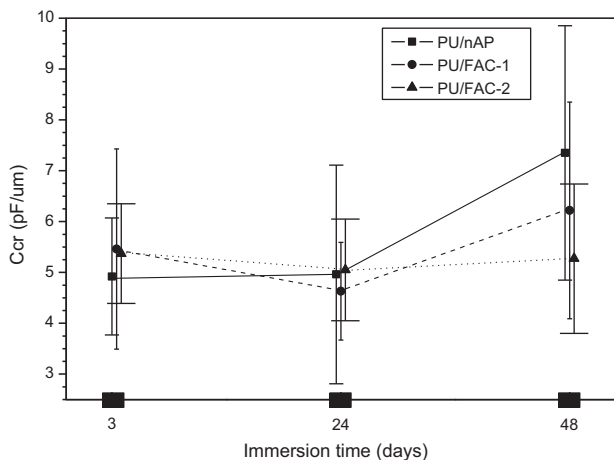


Fig. 11. Relative coat capacitance (C_{cr}) variation of coats during the immersion in an aqueous NaCl solution.

4. Conclusions

Conclusions of the test results of liquid 2K polyurethane paints and cured coats containing either nanosized aluminum phosphate (nAP) or microsized aluminum-zinc phosphate (FAC) with various dispersion additive content are as follows:

- paint with aluminum phosphate nanofiller exhibits significantly higher viscosity than compositions containing microsized aluminum-zinc phosphate. Additionally, higher dose of dispersing additive (i.e. 7.5 wt.parts/100 wt. parts of pigment and fillers) increases the viscosity of the systems based on mentioned filler types;
- coats containing aluminum phosphate nanofiller and higher amount of dispersing additive reach better adhesion to a steel substrate than similar coats filled with the same volume of microsized aluminum-zinc phosphate (PU/FAC-2). Polyurethane coats based on nanofiller exhibit slightly higher hardness than PU/FAC samples; the value of that parameter is not affected by dispersing additive content in the coating system;
- coats containing 9.8 wt.% of nanosized aluminum phosphate and higher amount of dispersing additive exhibit better anticorrosive properties (i.e. lower delamination around the scribe as well as higher blistering resistance) than similar samples based on either 12.2 or 15.6 wt.% of commercial aluminum-zinc phosphate micro-filler.

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