Self-crosslinking acrylic latexes containing nanoparticles ZnO with increased corrosion and chemical resistance of coating

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The requirements put on coating materials are more and more stringent mainly in the environmental domain, especially as regards VOC emissions. This is why water-based binders as alternatives to solvent-based binders, to provide paints possessing equally good use properties, are intensively sought. The objective of this work was to assess the anticorrosion and chemical properties of paint films based on new self-crosslinking acrylic latexes. The latexes were synthesized via two-step emulsion polymerisation to obtain a core-shell system. Nanostructural ZnO in an amount of 1.5 wt. % was added to the system during the latex binder synthesis. Paints with an enhanced corrosion resistance and chemical resistance of the films were prepared. The binders prepared were pigmented with anticorrosion pigments and their properties were compared to those of commercial water-based dispersions with either identical or different paint film formation mechanisms. The results gave evidence that if a well-selected pigment is used, the binders can be used to obtain anticorrosion coating materials for metallic substrates.

INTRODUCTION

Current legislation [1] aiming to reduce the volatile organic compound (VOC) contents in solvent-based paints along with a high toxicity of the traditional anticorrosion pigments are among the main reasons why alternative systems for the protection of metals are being sought [2]. The main group of environmentally friendly industrial paints includes water-based systems, high solid content systems and 100% solvent-free systems [3]. Binders for water-based paints are frequently manufactured by emulsion polymerisation. The benefits of emulsion polymerisation in industrial applications include environmental friendliness, possibility of obtaining polymers across a wide range of molecular weights, high polymerisation rates, good heat removal and a low reaction temperature [4]. Emulsion polymerisation using a "core-shell" system is a specific class: this technology is based on a specific molecular composition consisting of a hard core and soft shell. The dispersions are prepared by two-step polymerisation giving rise to heterogeneous particles containing regions possessing different compositions and properties. A polymer with a given composition is prepared during the first step, followed by preparation of another polymer, with a different composition, in the presence of the former polymer. Which part will be on the surface to constitute the coating (shell) of the particle and which part will be the core depends on a number of parameters, such as polarity of the phases, polymerisation thermodynamics and interphase tension [5,6]. Core-shell type polymeric particles find use in many applications, such as the printing industry, catalysis, pollution control, targeted transport of medicinal drugs in the body, impact modifiers and surface coatings. Added to paints, the particles may affect favourably the system's optical and physico-mechanical properties, e.g. increase its transparency to visible light or increase the surface hardness of the film. They can also find application in high-temperature thermal insulation coatings to reduce heat transfer (due to their low transparency for infrared radiation), and other [7, 8]. The polymers are usually prepared so as to obtain spherical particles: the first polymer constitutes the core of the polymer while the polymer prepared in the second step is incorporated into the outer layer to constitute the shell. The core can be liquid, solid or gaseous. The shell is usually solid and its properties depend on the target application. Micro or nano size particles can be prepared depending on the method of synthesis [9].

EXPERIMENTAL

Two-step emulsion polymerisation was used to synthesize two binders based on self-crosslinking acrylic latex. The following monomers were used for the synthesis of the binders: methacrylic acid (M_r = = 86.1 g mol^{-1}); methyl methacrylate (M_r = 100.1 g mol^{-1});

butyl acrylate (M_r = 128.2 g mol^{-1}); and acrylamide (M_r = 169.2 g mol^{-1}). Adipic dihydrazide (M_r = 174.2 g mol^{-1}) served as the crosslinking agent. All the above chemical were obtained from Sigma-Aldrich s.r.o., Czech Republic. Two binder types were prepared: one with ZnO nanoparticles (theoretical content 1.5 wt. %) (theoretical concentration, based on polymer content) added during the synthesis (labelled LZn), and a reference binder with no nanoparticles added, serving as the blank (labelled L0). The paint films using such binders are specific in that their formation includes post-crosslinking. The mechanism of the post-crosslinking process is based on a reaction between the carbonyl group present on the polymeric chain and the diamine dissolved in the aqueous component of the system.

The above binders were used to prepare anticorrosion paints for metals. Three anticorrosion pigments possessing different chemical compositions were selected for the paints:

- Mixture of $Al(PO_4)_3$ s $CaSiO_3$ (Heucophos® CAPP)
- Mixture of $Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2$ (Heucophos® CMP)
- $CaHPO_4$ (Heucophos® CHP)

In addition to the effect of the nanoparticles in the binder on the corrosion and chemical properties of the systems, the effect of the anticorrosion pigment was also examined. Pigment volume concentrations (PVC) 5% and 10% were used for this purpose. A silicate-based filler consisting of a mixture of SiO_2, (Mg,Fe,Li) $AlSi_3O_{10}(OH)_8$ and $Mg_3Si_4O_{10}(OH)_2$ (Plastorit Micro) was added to the system so that the PVC was increased invariably by 2%. Subsequently, a limestone-based filler ($CaCO_3$ – calcite, Omyacarb 2VA) was added to obtain the paint quotient Q = 100×(PVC/CPVC) = 50% (CPVC = = critical PVC) for all systems examined.

The corrosion properties of the paints prepared from the above binders were compared to those prepared from commercially available water-based binders. Binders with different paint film formation mechanism were selected: a styrene-acrylate copolymer drying by the physical mechanism (Axilat 2431, Synthomer a.s. – AX1), an urethanised alkyd emulsion drying by the oxypolymerisation mechanism (Hydrospol D 101, Synthomer a.s. – HDS), and an epoxy resin drying by the chemical mechanism (Epoxy 200 V55, Spolchemie a.s. – EPX).

Preparation of model paints and paint films for corrosion resistance tests

An aqueous high-concentration pigment paste was prepared in the first paint dispersing step. The liquid ingredients (distilled water, dispersing additives, coalescents and defoamers) were added to the dispersing vessel and the dispersing speed was set at 800 rpm. The pigments and fillers were homogenised in another vessel and added stepwise to the first vessel so that the powdered fraction was withdrawn by the stirrer continuously. Once all of the solid material had been added, the speed was increased to the maximum of 2500 rpm for 40-50 minutes. When a homogeneous paste free from any lumps resulted, the binder was added and the entire system was dispersed for another 15-20 minutes. The paints prepared were applied to steel panels (pre-cleaned and degreased with chloroform) for testing. The paints were applied to panels made (a) of steel class 11 (ISO 3574 CR1) and (b) of aluminium type 3003 H14 (Class 3, ISO 1514) based on the procedure as per CSN 673049 [10]. A box ruler with an adjustable slot was used for the application procedure. The films were conditioned for 15 days in an air-conditioned laboratory in standard conditions as per CSN EN 23270 [11].

Description of the materials

The basic properties of the pigments and binders were determined. The parameters determined for the pigments included density, measured by using an AccuPyc II 1340 pycnometer; the oil number, measured by the mortar-and-pestle method as per CSN EN ISO 787-5 [12]; and the critical pigment volume concentration (CPVC), calculated from the density and linseed oil consumption data. The parameters determined for the binders included density, measured pycnometrically as per CSN EN ISO 2811-1 [13]; pH (CSN EN ISO 787-9 [14]); viscosity (CSN ISO 2555 [15]), and the dry matter content (CSN EN ISO 3251 [16]). The data obtained are listed in Tables 1 and 2.

Tab. 1. Characteristic properties of binders

Binders	Viscosity [mPa.s]	pH [-]	Density [g/cm^{-3}]	Dry matter [%]
LZn	28	6.97	1.0291	43.86
L0	19	2.44	1.0131	51.23
AX1	510	7.87	1.0471	50.64
EPX	407	7.76	1.0831	55.02
HDS	39	5.34	1.0391	49.84

Tab. 2. Characteristic properties of pigments and fillers

Material	CPVC [-]	Oil consumption [g/100 g]	Density [g/cm^3]
H – CHP	44.85	39.72	2.8773
H – CAPP	44.51	44.58	2.6018
H – CMP	40.55	14.06	2.7991
Plastorit Micro	55.5	27.23	2.7373
Omyacarb 2 VA	56.12	24.99	2.8372

Testing methods

The following tests were made to examine the chemical and anticorrosion properties of the paints:

Corrosion test in salt spray atmosphere (CSN EN ISO 9227 [17]) – The paints were applied to steel panels 152 × 102 × 0.8 mm size. The ruler slot width was 250 μm and 4 layers were consecutively applied in 3-day intervals. The final dry film thickness (DFT), determined as per CSN EN ISO 2808 [18], was 100 ± 10 μm. A straight cut 1 mm wide was made through each dry film. The samples were left in the salt spray atmosphere for 120, 240 and 360 hours, respectively. The parameters measured after the exposure included corrosion near the test cut (ASTM D 1654-92 [19]), blistering (i.e. osmotic bubble formation) of the paint film (ASTM D 714-87 [20]), corrosion on the steel panel area and metal corrosion effects observed on the paint film surface (ASTM D 610-08 [21]).

The paint film's total anticorrosion efficiency score was obtained from the scores for the partial corrosion effects. The underlying assumption was that a high-quality anticorrosion paint containing an efficient anticorrosion pigment shows no blistering because the ingredients are water-insoluble. We assume that the anticorrosion pigment acts in the anodic or cathodic corrosion regions, owing to which the coating does not corrode in the test cut areas and no corrosion occurs on the metal substrate beneath the coating. The scores were assigned within the range from 1 (low anticorrosion efficiency) to 100 (high anticorrosion efficiency), and the total anticorrosion efficiency score was obtained as the arithmetic mean of the partial scores. The scores were determined for different exposure periods and served to select systems that are most suitable for the given binders [22, 23].

Accelerated cyclic test with exposure to a salt spray atmosphere alternating with temperature changes (CSN 67 3098 [24]; CSN EN ISO 9227) – Paint film adhesion was measured in addition to the corrosion effects. The paints were applied onto steel and aluminium panels 152 × 102 × 0.8 mm size to form films with DFT = (95 ± 10) μm. One test cycle consisted of the following 4 partial 24-hour cycles: (1) exposure to neutral salt fog, (2) heating at 60 °C in a dryer, (3) exposure to a salt fog again, and (4) exposure to a frost of –20 °C.

Chemical resistance to methyl ethyl ketone (ASTM D 4752-10 [25]) – The paints were applied to glass panels 200 × 100 × 5 mm size by using a box ruler at a slot width of 150 μm. The DFT was 60 ± 10 μm. Resistance to MEK was measured in 50 seconds, after which the assessment was made based on the assessment table included in the above standard, and in 300 seconds, after which the number of double rubs was measured (1 double rub ~ 1 second).

RESULTS AND DISCUSSIONS

Results of the corrosion test in the salt spray atmosphere (CSN EN ISO 9227)

The corrosion effects referred to above were assessed, the results observed in 360 hours are listed in in Table 3.

The corrosion effects were evaluated in dependence on the time of exposure (Figs. 1 and 2) and used to determine the anticorrosion efficiency scores. The anticorrosion efficiency of the binder LZn approached closely to that of the conventional alkyd or epoxy resin dispersions. This anticorrosion efficiency was higher than that of the reference binder L0, thus giving evidence that the ZnO nanoparticles incorporated in the dispersion have a favorable effect on the anticorrosion efficiency. The binder LZn also exhibited a higher resistance than

Tab. 3. Results of corrosion after exposures in 5% fog of NaCl (The results for both PCV values (5% / 10 %) are written in one line)

Binders	Anticorrosion pigment	Corrosion in cut [mm]	Corrosion of metal substrate [%]	Rusting on surface paint film [%]	Osmotic blisters of paint film [-]
LZn	H-CMP	0.5 / 0.1	33 / 33	16 / 33	6MD / 6D
	H-CHP	0,3 / 0	33 / 33	33 / 33	6MD / 6MD
	H-CAPP	0.2 / 0	16 / 33	16 / 16	6MD / 6MD
L0	H-CMP	0.7 / 0.1	50 / 50	16 / 50	6MD / 6MD
	H-CHP	0.5 / 0.2	50 / 33	33 / 50	6D / 6D
	H-CAPP	0.3 / 0	33 / 33	16 / 33	6MD / 6D
AX1	H-CMP	2.4 / 0.5	50 / 50	50 / 50	6MD / 6MD
HDS	H-CMP	3.4 / 2.8	16 / 16	16 / 10	4MD / 2MD
EPX	H-CMP	3.1 / 3.0	50 / 50	0.01 / 0.01	6M / 8F

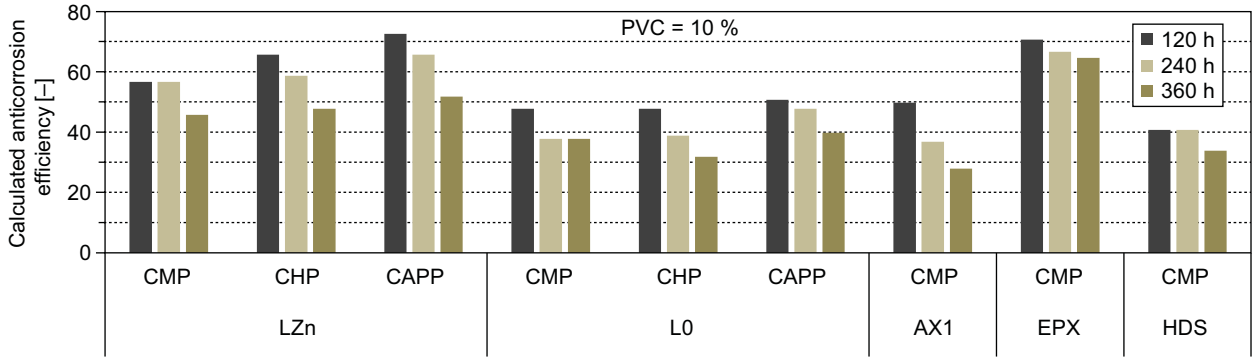

Fig. 1. Dependence of anticorrosive anti-corrosion coating on time of exposure in corrosion environment for PVC 10 %

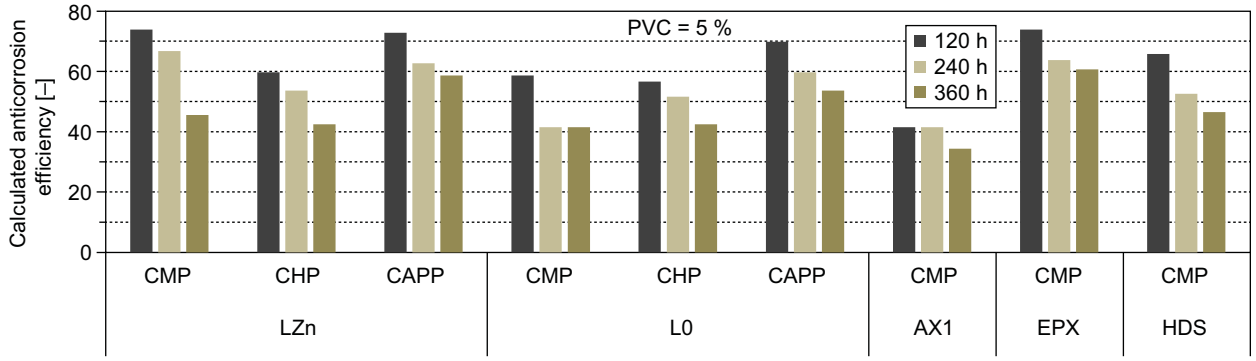

Fig. 2. Dependence of anticorrosive anti-corrosion coating on time of exposure in corrosion environment for PVC 5 %

the styrene-acrylate type binder. Corrosion product formation near the test cut in the paint film was also considerably less pronounced with the paints based on the LZn binder than with the paints based on the L0 binder. We ascribe this to the presence of the homogeneously dispersed ZnO nanoparticles, which also improved appreciably paint film adhesion and chemical resistance. As expected, the total protective efficiency decreased in time. Generally, the anticorrosion efficiency was higher for the films with PVC = 5 % than for the films with PVC = 10 %. The highest anticorrosion efficiency scores were obtained when using the Heucophos CAPP pigment (at both PVC levels).

Results of corrosion resistance testing after exposure to the salt spray atmosphere alternating with temperature changes

The corrosion effects and adhesion parameters after 3 cycles for the samples tested on steel panels are

Tab. 4. The results of the cyclic test of corrosion resistance after 3 cycles – the results for both PCV values (5 % / 10 %) are written in one line – on the steel substrate

Binders	Anticorrosion pigment	Corrosion in cut [mm]	Corrosion of metal substrate [%]	Osmotic blisters of paint film [-]	Cross-cut test [-]
LZn	H-CMP	0 / 0	33 / 33	6M / 6M	0 / 0
	H-CHP	0 / 0	33 / 16	6M / 6MD	1 / 1
	H-CAPP	0 / 0	33 /16	8M / 8MD	1/ 0
L0	H-CMP	0 / 0.05	50 / 33	8MD / 8D	2 / 2
	H-CHP	0.15 / 0.2	50 / 50	8MD /8M	2 / 1
	H-CAPP	0.05 / .2	50 / 50	8MD / 8D	1 / 2
AX1	H-CMP	0.5 / 0.7	50 /33	8D / 8MD	2 / 2
HDS	H-CMP	–	–	–	5 / 5
EPX	H-CMP	–	–	–	5 / 5

listed in Table 4 and the adhesion and blistering characteristics on aluminium panels are listed in Table 5.

The films based on epoxy and alkyd resin binders lost their adhesion to both metals as early as the first cycle and so their corrosion efficiency could not be evaluated and their adhesion was scored 5. The paint based on the binder LZn exhibited the highest degree of adhesion (cross-cut test CSN EN ISO 2409 [26]) 0, which means that the cuts following the cross-cut test were completely smooth and none of the squares was damaged. The adhesion to the steel panel was also excellent.

Tab. 5. The results of the cyclic test of corrosion resistance after 3 cycles – the results for both OKP values (5 % / 10 %) are written in one line – on the aluminum substrate

Binders	Anticorrosion pigment	Osmotic blisters of paint film [-]	Cross-cut test [-]
LZn	H-CMP	8F / 6F	0 / 1
	H-CHP	6M / 6F	2 / 2
	H-CAPP	6F / F	1 / 1
L0	H-CMP	8F / 6F	2 / 2
	H-CHP	6F / 6M	1 / 2
	H-CAPP	6F / 4M	5 / 5
AX1	H-CMP	6F / 8F	1 / 2
HDS	H-CMP	–	5 / 5
EPX	H-CMP	–	5 / 5

Results of chemical resistance testing – MEK test (ASTM D 4752-10)

The samples based on the LZn binder exhibited a high resistance to MEK, comparable to that of the most resistant epoxy resin-based paints (Table 6). This resistance was substantially higher than that of the paint based on reference binder L0 with no nanoparticles, thus giving evidence of the favourable role of the ZnO nanoparticles. Presumably, this is due to the existence of complex bonds between the Zn^{2+} cations and the carboxy groups present on the polymer chains. The damage in the case of the LZn binder in 50 sec was categorised as Class 4, i.e. the paint film was not appreciably disturbed, only the surface was polished slightly.

CONCLUSIONS

The anticorrosion properties of the paint films were characterised in terms of the anticorrosion efficiency of the paint and of the pigment in dependence on the duration of exposure to a corrosion environment. It was concluded that waterborne binders based on self-crosslinking acrylic latex with incorporated ZnO nanoparticles can be pigmented and used for paints with enhanced anticorrosion efficiency usable in environments with the maximum corrosion aggressiveness C3. The anticorrosion efficiency was appreciably higher than in the case of the binder AX1 and basically comparable to that of the binder HDS. The epoxy binder, however, was superior to the LZn binder, the films with that binder exhibited anticorrosion efficiency levels 10% to 15% (in the average) higher. The chemical resistance in the MEK test was also very good, comparable between the LZn binder and the epoxy resin-based binder.

It is concluded that water-based paints should not be regarded just as materials with poor anticorrosion and chemical properties: instead, they should be regarded as materials worth understanding because they show promise owing to their favorable properties, as outlined in the introduction. Forthcoming tests will be focused on their properties in combination with other pigments, in the form of hybrid systems or for use as topcoats.

Tab. 6. Results of the MEK test 28 days after coating – the results for both OKP values (5 % / 10 %) are written in one line

Binders	Anticorrosion pigment	Resistance at 50 seconds [-]	Resistance at 300 seconds [max. number of double rubs]
LZn	H-CMP	4 / 4	253 / 207
	H-CHP	4 / 4	300 / 300
	H-CAPP	4 / 4	300 / 300
L0	H-CMP	1 / 0	55 / 46
	H-CHP	2 / 1	75 / 61
	H-CAPP	2 / 0	67 / 43
AX1	H-CMP	3 / 2	98 / 91
HDS	H-CMP	0 / 0	34 /26
EPX	H-CMP	3 / 3	278 /256

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