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WATERBORNE COATINGS BASED ON ACRYLIC LATEX CONTAINING NANOSTRUCTURED ZnO AS AN ACTIVE ADDITIVE

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Summary

This work was devoted to the study of the properties of an acrylate latex-based binder synthesised by semi-continuous emulsion polymerisation. Nanoparticles of zinc oxide (NPsZnO) in an amount of 1.5 wt.% with respect to the polymer content were added to the binder during the synthesis procedure. The binder was then homogenised with various anticorrosion pigments, fillers and additives to obtain model anticorrosion paints. In addition, model paints with expected enhanced antimicrobial resistance designed for the protection of mineral substrates were also formulated and prepared. The effects of NPsZnO on the physico-mechanical properties and on the chemical, anticorrosion and antimicrobial resistance of the paint films were examined. The properties of the paints based on the synthesised binders were also compared to those of a commercial acrylate-type binder. The results show that incorporation of NPsZnO into the latex during the synthesis provided stable polymeric dispersions exhibiting physico-chemical, mechanical and anticorrosion properties that were superior to those of a blank binder (containing no nanoparticles) as well as to the commercial binder. It was also demonstrated that the binder with NPsZnO provided anticorrosion paints that are usable as coatings for environments with a moderate corrosion burden as well as paints for interior applications with reduced biocide contents.

Key words: acrylic latex, antimicrobial coating, flash rust, zinc oxide nanoparticle, anticorrosion coating

1 Introduction

Waterborne paints are generally regarded as good filling binder materials.^{1,2} The quality of surfaces finished with such paints is typically adequately high.³ The fact that a wide number of paint application methods can be used is a major advantage.⁴ The mechanical resistance of single-component paints and their resistance to fluids are often poor.⁵ Hence, two-component or UV-curable coating systems are generally required.⁶ In the case of single-component latex-based paint films, the physico-mechanical properties and chemical resistance can be improved by introducing keto-hydrazide interparticle crosslinking into the latex binder.⁷ The crosslinking mechanism usually depends on the reaction between the carbonyl groups present in the polymeric latex and diamine dissolved in the aqueous component. The carbonyl group carrier is usually diacetone acrylamide, incorporated into the system during the synthesis by emulsion polymerisation as a co-monomer.⁸ A small amount of a diamine, specifically dihydrazide, must be added to the synthesised latex for successful crosslinking. Adipic acid dihydrazide is usually used as the compound with hydrazide groups (-NH-NH₂), typically in the form of an aqueous solution at a concentration of 10% (w/w) in a stoichiometric ratio to diacetone acrylamide to provide the single-component self-crosslinking system.^{9,10}

Optimum ambient humidity and temperature must be maintained during the latex-based paint application procedure: if the humidity is too high, water evaporates slowly and defects develop,¹¹ whereas too low humidity means that paint film drying occurs too rapidly.¹² Flash corrosion usually takes place if the drying waterborne film is exposed to highly humid air.¹³ Paint film formation by latex-

based paints during water evaporation proceeds by the coalescence of polymeric particles, their deformation and, finally, diffusion of the polymeric chains between particles.¹⁴ If water evaporation from the latex film is slowed down by high air humidity, the particle coalescence process is preceded by soluble iron salt extraction into the paint film. These ions can diffuse as far as the paint film surface, thereby spoiling the coating.^{15,16}

Frequently, waterborne paint is affected by microorganisms, which can alter the properties of both the liquid paint and the final coating.^{17,18} Liquid paint may start losing its viscosity, release gases and change its colour or pH.¹⁹ Microbial colonisation of the paint film surface is primarily an aesthetic issue, although bubbles may also form and the film may peel off or be degraded altogether.²⁰ The sensitivity of a paint film to microorganisms partly depends on the chemical nature of the binder and on the pigment type and concentration. The presence and concentration of antimicrobial agents play major roles in determining the sensitivity of the paint to microbiological action.²¹ Such agents consist of a large number of different organic as well as inorganic ingredients. The key inorganic ingredient imparting paint with long-term protection against moulds is zinc oxide (ZnO).^{22,23} Antimicrobial paints are designed to reduce the risk of infection propagation in hospitals and doctor's offices, public offices, food industry facilities and other buildings visited by the public and should be active for several years.²⁴ They are also used to protect outdoor surfaces such as facades, boat and ship bottoms, railings, etc., against moulds.²⁵

Acrylate-based latexes are among the modern binders used for industrial coatings compatible with VOC for wood, metals and plastics.²⁶ The acrylic latex formula was selected to best satisfy the specific requirements for application properties.²⁷ The resulting polymeric dispersions possess a very low viscosity and the latex particle size is about 0.2 μm , thus they are typically slightly bluish.²⁸ The non-volatile content is typically 40% to 50%. Surfactants are usually added to ensure good stability of such finely dispersed systems.²⁹ A high resistance to freezing/thawing cycles and better wettability of the pigments is achieved by introducing 1-2% acrylic or methacrylic acid into the monomer feed.³⁰ The emulsion polymerisation process is used most frequently for the synthesis of acrylic dispersions, as it is environmentally friendly and can be used to prepare a wide range of polymeric dispersions.^{31,32}

The objective of this work was to prepare and investigate the properties of new waterborne paints based on acrylic latex containing NPsZnO. Owing to the presence of these nanoparticles, the paints were expected to possess antimicrobial activity, favourable physico-mechanical properties and chemical resistance of the resulting coating films. Further, the paints were formulated to obtain increased corrosion resistance and resistance against flash corrosion. The effects of NPsZnO in the synthesised latex binder on the final properties of the paint films were investigated and compared to a commercially available acrylic binder.

2 Experimental methods and materials

2.1 Preparation of latexes

The following monomers were used for the synthesis of latex binders: methacrylic acid (MAA, $M_r = 86.1$ g/mol), methyl methacrylate (MMA, $M_r = 100.1$ g/mol), butyl acrylate (BA, $M_r = 128.2$ g/mol) and diacetone acrylamide (DAAM, $M_r = 169.2$ g/mol) (all Sigma-Aldrich, Germany). Adipic acid dihydrazide (ADH, Sigma-Aldrich, Germany) served as the crosslinking agent. Ammonium persulphate (APS, 99.9% Lach-Ner, Czech Republic) and Disponil FES 993 (BASF, Germany) were used in the synthesis process as the initiator and the emulsifier, respectively. NPsZnO (trade name NanoTek[®], 99.9%, $d_{50} = 40\text{-}100$ nm) (LZnO) was purchased from Alfa Aesar (USA).

Two latex binders differing in the presence of NPsZnO were synthesised by a semi-continuous emulsion polymerisation using a variable content of acrylic monomers. To provide good physico-

mechanical properties and chemical resistance of resulting coatings, DAAM was incorporated in with the polymer particles to introduce ketone carbonyl functional groups capable of undergoing subsequent inter-particle crosslinking with a hydrazide-based crosslinking agent. To maintain a colloidal stability of the latex during the polymerisation procedure and to prevent increased coagulum formation, a two-stage polymerisation process was performed, where the nanopowder was dosed in the second step. The latex binder labelled L0 was free from NPsZnO and the latex binder labelled LZnO comprised 1.5 wt.% of ZnO nanoparticles (theoretical concentration, based on polymer content). The detailed composition of monomer feeds forming both latexes was as follows: 42 g MMA, 53 g BA and 5 g MAA dosed in the first step and 41 g MMA, 52 g BA, 2 g MAA and 5 g DAAM dosed in the second step.

The latexes were produced in a 700 ml glass reactor under a nitrogen atmosphere at 85°C. The reactor charge was put into the reactor and heated to the polymerisation temperature. Then, the monomer emulsion was fed into the stirred reactor at a feed rate of about 2 ml/min in two steps (a 15-minute-long period between the two feeding steps was used). After that, the polymerisation was completed during 2 hours of the hold period. The recipe for emulsion polymerisation is shown in Table 1. The pH value of the latexes was adjusted to 8.5 by adding ammonia solution. The theoretical solid content of the latexes was about 42 wt.%. After the synthesis, filterable solids were dried and weighed and the coagulum content was calculated according to $\text{Coagulation (\%)} = 100 \times M_f / (\text{real solids content} \times M_E + M_f)$, where M_f and M_E are weights of dried filterable solids and the filtered emulsion, respectively.

For the preparation of the latex LZnO, the above-mentioned procedure included the preparation of well-dispersed NPsZnO aqueous suspension. Firstly, ZnO nanopowder was mixed with water and the emulsifier that were designated for the preparation of the second step monomer emulsion. To destroy agglomerates formed by individual NPsZnO to a great extent, proper dispersing using an ULTRA-TURRAX T25 disperser (IKA, Germany) at 14 000 rpm was performed for 20 min followed by ultrasonic treatment for 1 hour. Then, the finely dispersed NPsZnO suspension was gently mixed with the monomers designated for the preparation of the second step monomer emulsion (using a stirrer at low speed for 1 minute). Finally, the resulting second step monomer emulsion containing NPsZnO was dosed into the reactor immediately.

Table 1 Recipe for emulsion polymerisation of latex binders L0 and LZnO

	Reactor charge	Monomer emulsion (1 st step)	Monomer emulsion (2 nd step)
Water (g)	70	75	125
Disponil FES 993 (g)	0.5	7.4	7.4
APS (g)	0.4	0.4	0.4
Monomers (g)	-	100	100
NPsZnO ^a (g)	-	-	1.5

^a The component was used only in the case of LZnO synthesis.

2.2 Formulation and preparation of the pigmented paints

The synthesised binders were used to formulate anticorrosion paints intended for corrosion protection of metallic substrates and interior paints intended for the protection of mineral substrates. Five pigment types with different chemical compositions and different protective effects were selected for the anticorrosion paints designed for application onto metallic surfaces. Two pigments possessed the barrier protection property: talc, a clay mineral consisting of hydrated magnesium silicate $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ (pH 7.0-7.3, $d_{50} = 10\text{-}12 \mu\text{m}$, trade name Talc SA-20, Naintsch, Austria) with lamellar particles, and wollastonite, a calcium inosilicate mineral CaSiO_3 (pH 10.1, $d_{50} = 16\text{-}28 \mu\text{m}$, trade name Wollastonit K 1025, MINKO, Czech Republic) with needle-shaped particles. Three anticorrosion

pigments acted by the electrochemical or chemical protection mechanism: a calcium aluminium polyphosphate silicate hydrate as a mixture of $\text{Al}(\text{PO}_4)_3$ s CaSiO_3 (pH 8.1, d_{50} = 2-4 μm , trade name Heucophos® CAPP, Heucotech, Germany), and a calcium magnesium orthophosphate as a mixture of $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Mg}_3(\text{PO}_4)_2$ (pH 6.5, d_{50} = 2-3 μm , trade name Heucophos® CMP, Heucotech, Germany). A calcium hydrogen phosphate CaHPO_4 (pH 7.6, d_{50} = 1-2 μm , trade name Heucophos® CHP, Heucotech, Germany) was the third type used. The pigments were added to the system at a pigment volume concentration (PVC_{pig}) 10%. The anticorrosion paints were pigmented with fillers so as to hold the PVC/CPVC ratio (CPVC = critical PVC) constant at 0.5. One of the fillers was a specific blend of silicon oxide SiO_2 , chlorite type mica (Mg , Fe , Li) $\text{AlSi}_3\text{O}_{10}(\text{OH})_8$ and talc $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ (trade name Plastorit® Micro, Imerys, Austria). Limestone CaCO_3 (calcite, trade name Omyacarb 2VA, Omya, Czech Republic) served as another filler. The structures of the pigments and fillers are shown in Figs. 1-3. The structures were obtained on a JEOL JSM 5600 LV (JEOL Ltd., Japan) scanning electron microscope (SEM).

Apart from the examination of the effect of NPsZnO on the physico-mechanical, chemical and anticorrosion properties of coating films, the coating properties were compared to those based on the commercially available aqueous dispersion of a styrene-acrylate copolymer (trade name Axilat 2431, Synthomer, Czech Republic) (AX1) dispersed with the anticorrosion pigment Heucophos® CMP.

The effect of NPsZnO on the antimicrobial properties of the coating films was investigated on model interior pains intended for the protection of mineral substrates. The combination of the pigment ZnO (zinc oxide; zincite, Sigma-Aldrich, Germany) at PVC = 13% and TiO_2 (titanium oxide; anatase, Prechezia, Czech Republic) at PVC = 2% was used, and a limestone-base filler (CaCO_3 ; calcite, Omyacarb, 2VA, Omya, Czech Republic) was added to adjust the paint's PVC/CPVC ratio to 1.10. The antimicrobial paints were tested as such and with the addition of the biocide bis(2-pyridylthio)zinc-1,1'-dioxide (trade name Zinc Omadine, Arch Chemicals, Germany) (ZO) at 0.1 wt.% and 0.3 wt.%.

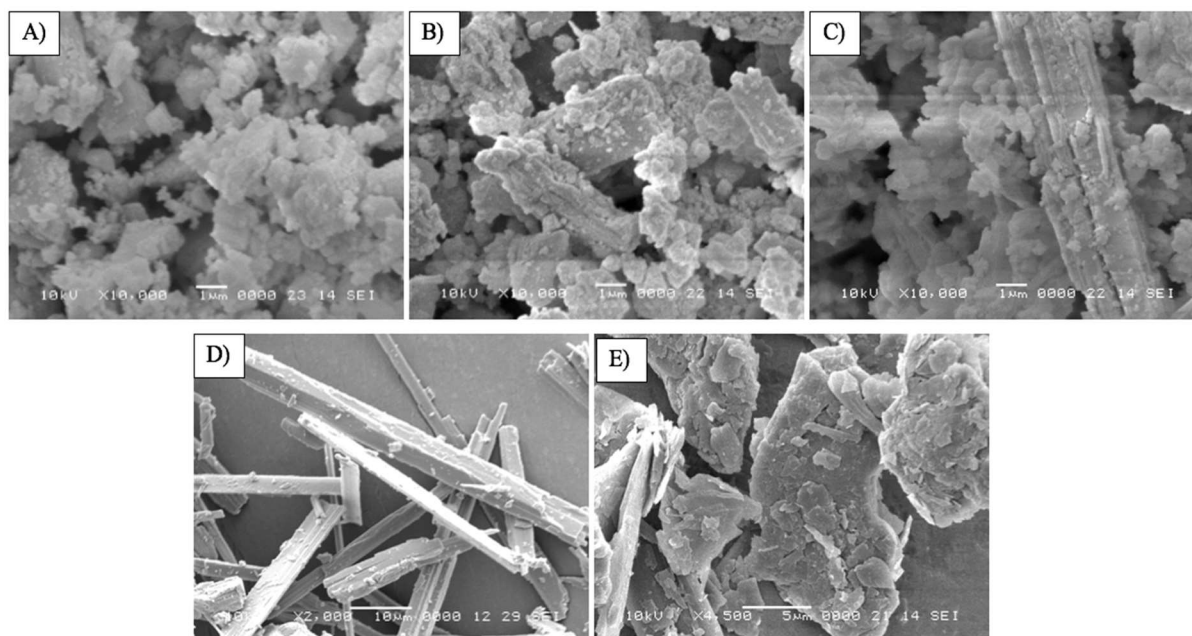


Figure 1 Structure of anticorrosive pigments at different magnification - SEM A) Phosphate Ca, B) Phosphate Ca/Mg, C) Phosphate Al/Mg/Ca, D) Wollastonit, E) Talc

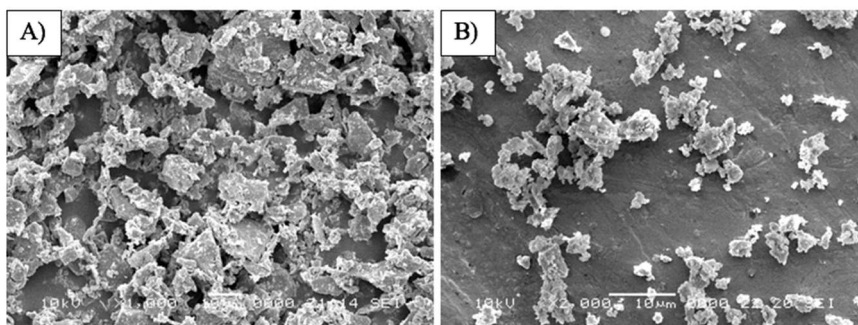


Figure 2 Structure of fillers with different magnifications - SEM A) Plastorit micro B) CaCO₃ – calcit

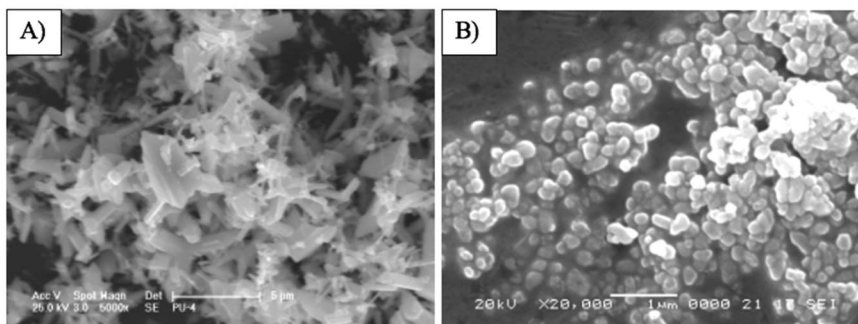


Figure 3 Structure of white pigments with different magnifications - SEM A) ZnO - zincite B) TiO₂ - anatase

2.3 Preparation of paint films samples

Films of the model paints were prepared for testing. The paints were applied to glass and steel panels as required for each testing method. A box ruler with an adjustable slot was used to prepare films at any desired thickness. The physical and chemical properties were studied on paint films applied to glass panels 5 mm x 50 mm x 100 mm size, ruler slot 150 μm. The anticorrosion and mechanical properties were studied on paint films applied to steel panels (steel class 11 - ISO 3574 CR1), ruler slot 250 μm. The steel panel size was 0.8 mm x 51 mm x 102 mm for the mechanical resistance tests and 0.8 mm x 102 mm x 152 mm for the flash corrosion tests. The films were conditioned for 15 days in an air-conditioned laboratory in standard conditions as per ČSN EN 23270.

The antimicrobial resistance was investigated on films applied to filter paper (Munktell Filtrak 391, Munktell & Filtrak, Germany) 15 cm in diameter and 84 g/m² grammage. Four film layers were applied with a brush (in alternating directions). The delay between the applications of the layers was approximately 3 hours. The filter paper was cut into squares 4 cm x 4 cm. The paint films were sterilised by UV radiation for 15-20 minutes and then put on a Petri dish with a meat-peptone agar (HIMEDIA, India), oriented with the functional paint surface up.

The paints were prepared by a two-stage dispersing process on a dissolver disperser (Dispermat, Donventa AG, Switzerland). A highly concentrated aqueous pigment paste was prepared during the first stage. The liquid materials were added to the dispersing vessel, i.e. distilled water and dispersing additives, one based on Hydropalat 3043 sodium acrylate (Henkel, Germany) and the other based on the Hydropalat 1080 mono functional alkylene oxide block copolymer (Henkel, Germany), Bentone EW rheological additive (smectite clay, Elementis, Germany), and Dehydran 1293 modified polysiloxane based defoamer (Henkel, Germany). The disperser speed was 1500 rpm. Another vessel was for the homogenised pigments and fillers, which were added slowly to the vessel with the aqueous ingredients so that the powder moiety was withdrawn continuously. After all the powder had been added, the speed was increased to the maximum of 2500 rpm and the mixture was allowed to be dispersed for 40-50

minutes. When a homogeneous paste was formed, the binder was added and the dispersion process was resumed for 15-20 minutes.

3 Testing methods

3.1 Determination of the characteristic properties of the pigments, fillers and binders

The binders were characterised by their density (determined pycnometrically as per ČSN EN ISO 2811-1), pH (measured with a HANNAH I 8424 pH meter, HANNA Instrument, USA), viscosity (RotoVisco - RT10 rotary viscometer, Haake Technik, Germany), dry matter content (determined as per ČSN EN ISO 3251) and minimum film forming temperature (MFFT) (MFFT 60, Rhopoint Instrument, UK). The actual nanoparticle content in the binder LZnO was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) on a ThermoScientific iCAP 7000 Series ICP spectrometer. The samples were measured in the aerosol form at a flow rate of 1.5 ml/min, Ar plasma input power 1000 W. The critical pigment volume concentrations (CPVCs) were calculated for the pigments and fillers based on their densities (AccuPyc II 1340 gas pycnometer, Micromeritics, USA) and oil consumption (mortar-pestle method, ČSN EN ISO 787-5).³³

3.2 Physical-mechanical and chemical properties of the prepared coatings

3.2.1 Paint film hardness determination by the Buchholz indentation test (ČSN EN ISO 2815)

The hardness of the paint films is routinely determined by the indentation method using an indenter with a specific shape. The final dry film thickness (DFT), determined as per ČSN EN ISO 2808, was $60 \pm 10 \mu\text{m}$. The hardness was measured on a Buchholz Tester (Byk-Gardner, Germany); the weight put on the indenter was $500 \pm 5 \text{ g}$, with a contact time with the sample of $35 \pm 5 \text{ sec}$. The film hardness was determined via the indentation length in mm, which is inversely proportional to the paint film hardness ($100/L$ where L is the true indentation width in mm).

3.2.2 Determination of paint film mechanical and chemical resistance

Mechanical resistance was measured on paint films with $DFT = 55 \pm 10 \mu\text{m}$. The films were subjected to the following tests: cross-cut test as per ČSN EN ISO 240 on an Elcometer 1542 cross-hatch adhesion tester to determine the film adhesion; cupping test on an Elcometer 1620 cupping tester for determining the resistance of the paint film as per ČSN EN ISO 1520; bend test on an Elcometer 1506 cylindrical mandrel bend tester to determine the paint film resistance to bending as per ČSN EN ISO 1519; and the impact test on an Elcometer 1615 impact tester to determine the paint film impact resistance as per ČSN EN ISO 6272-1. All the Elcometer instruments are products of Elcometer Instruments, Germany. The chemical resistance of the paint films was determined by exposing the films to methyl ethyl ketone as per ASTM D 4752-10.

3.3 Anticorrosive properties of coating films

3.3.1 Accelerated laboratory test to examine flash corrosion

Typical mainly for waterborne paints, flash corrosion is one of the unwanted effects associated with paint application. Corrosion of this type occurs if the paint film is allowed to dry at a high relative humidity. This effect can be prevented by using inhibitors. The paints were applied to steel panels using a box ruler with a slot $250 \mu\text{m}$. The coating films prepared were allowed to dry at room temperature ($23 \pm 2^\circ\text{C}$) and $45 \pm 5\%$ relative humidity for 2 hours and then put into a cooling chamber at 5°C for

16 hours. Subsequently the samples were removed from the chamber and covered for 2 hours with filter paper wetted in distilled water. Finally, the samples were dried and flash corrosion was assessed as per ASTM D 610.³⁴

3.3.2 Corrosion test in condensation-water atmosphere (ČSN EN ISO 6270-2)

The corrosion resistance of the paint films and the effect of NPsZnO on the anticorrosion properties were examined on paint films samples DFT $145 \pm 10 \mu\text{m}$. A straight test cut 80 mm long and 1 mm wide was made in each dry film. The samples were left in the condensation-water atmosphere for 480 hours. The effects subsequently assessed included corrosion near the test cut (ASTM D 1654-92), the formation of osmotic blisters (on the paint film (ASTM D 714-87), corrosion of the metal substrate and the effects of substrate metal corrosion on the paint film (ASTM D 610).

The overall protective efficiency of the paint films was assessed by combining the partial resistance scores for each corrosion type into a total score. In more detail, an anticorrosion resistance score within the range of 1-100 where 1 denotes low anticorrosion efficiency and 100 denotes high anticorrosion efficiency was assigned to each corrosion type, and the total score was calculated as the arithmetic mean of the partial scores. This total score described the efficiency of a paint for various periods of exposure to a specific corrosion environment.^{35,36}

3.4 Antimicrobial properties of the coating films

3.4.1 Testing paint film antibacterial and antifungal resistance

A suspension of bacteria with McFarland score 1 (3×10^8 CFU/ml) in sterile saline (0.9% NaCl, Lachema, Czech Republic) was prepared and diluted to the working concentration 1×10^5 CFU/ml, and 0.1 ml aliquots were applied and spread onto paint film samples in Petri dishes (\varnothing 85 mm). The dishes were put into a BT 120M biological thermostat (Systec, Germany) heated at 37°C for 24 hours. Control samples were created by pressing a square of the paint film onto a clean dish with agar. The dishes were then put into the thermostat again (37°C/24 hours). Finally, the imprints were evaluated to determine the antimicrobial efficiency of the paint films in %.

Well-spored cultures were prepared to assess the binder's antifungal properties. Moulds were cultured on malt agar at 25°C for 5-7 days. Subsequently, a mould suspension was made up and applied to the sample surface as described above for the antibacterial effects. Samples inoculated with the moulds were incubated at 24-25°C for 5-7 days, after which the antifungal efficiency (%) was evaluated based on the sample area affected by the microbial colonies.^{37, 38}

4 Results and discussion

4.1 Determination of the characteristic material properties

The characteristic properties of the pigments and fillers used to prepare the paints for metals and mineral material are listed in Table 2. Oil consumption generally depends on the pigment particle heterodispersity, size, shape and specific surface area³⁹, so the observed data lie within the wide region of 25.34 to 59.51 $\text{g}_{\text{oil}}/100\text{g}_{\text{pigment}}$. Each pigment was measured in five replicates and the arithmetic mean was tabulated. Generally, oil consumption increases with decreasing crystal orientation and increasing surface activity.⁴⁰ Pigment densities were determined by a gas pycnometer with a precision of 0.0001 g/cm^3 . The majority of the data lay within the range of 2.7-3.1 g/cm^3 ; only ZnO exhibited a higher density (5.6512 g/cm^3) and possessed a low CPVC (24.29). The CPVC was calculated based on the known linseed oil consumption and density and was calculated as a dimensionless quantity.

Table 2 *Characteristic properties of pigments and fillers*

Material	CPVC [-]	Oil consumption [g/100g]	Density [g/cm³]
Wollastonite	49.46	32.71	2.9042
Talc	35.62	59.51	2.8217
Phosphate Ca	40.85	39.73	2.8773
Phosphate Mg/Ca	38.43	53.21	2.7991
Phosphate Si/Al/Ca	44.51	44.58	2.6018
ZnO (zincite)	24.29	52.03	5.6512
TiO₂ (anatase)	47.66	33.17	3.0781
Natural mixed silicate filler	55.51	27.23	2.7373
CaCO₃ (calcite)	49.21	25.34	2.7237

Table 3 lists the characteristic properties of the binders, specifically viscosity, density, pH, dry matter content and MFFT. The dry matter contents of all binders lay within the range from 40 to 55%. The pH of the binder LZnO was highest (6.07) and approached that of the reference binder AX1 (5.98). The pH of the synthesised binder L0 was substantially lower, at 1.78. The increase in pH induced by the presence of NPsZnO may beneficially reduce flash corrosion and/or improve the stability of the dispersion itself (the keto-hydrazide reaction is acid catalysed). The viscosity of the binders was appreciably different, and that of the synthesised binders was much lower than that of the reference binder. The last parameter measured was the MFFT, which was substantially lower for the synthesised binders (5.8°C to 7.1°C) than for the AX1 styrene-acrylate type binder (23.4°C). This was highly beneficial in the paint film preparation because no coalescing additives had to be used.⁴¹ It should be noted that the LZnO binder contained 0.7% of coagulum after synthesis (in contrast to the coagulum-free L0 binder). Therefore, the real concentration of NPsZnO in the coating films was expected to be lower than the theoretical one (1.5 wt.%). This assumption was confirmed by ICP-OES measurements, which revealed that the real content of NPsZnO in the LZnO-based latex coatings was about 1.223 wt.%.

Table 3 *Characteristic properties of binders*

Binder	Viscosity [mPa.s]	pH	Density [g/cm³]	Dry matter [%]	MFFT [°C]
LZnO	24.58	6.07*	1.02	43.86	7.1
L0	15.56	1.78*	1.01	40.23	5.8
AX1	230.13	5.98	1.04	50.64	23.4

* pH after the synthesis of the latex

4.2 Hardness evaluation – Buchholz indentation test

The hardness values of the anticorrosion paints determined based on the indentation length (in mm) according to Buchholz were measured in dependence on time: the first measurement was made 1 day after paint application; subsequent measurements were made in 7-day intervals for 42 days. For all binders, every next hardness measured was about 15% ± 5% higher than the previous value (during the first two weeks), to converge to a constant value approximately in 21 days. Table 4 lists the hardness values measured in 1, 14 and 28 days after application. It was found that the paint films based on the binder LZnO exhibited greater hardness, probably due to ionic bonds that formed between the carboxylate latex polymer and dissociated Zn²⁺ ions. The highest value (87) was observed for the LZnO binder containing the silicate-based pigment (wollastonite).

Table 4 Hardness of the anticorrosion coating films – Buchholz indentation test

Binder	Anticorrosive pigment	Hardness of paint film [100/L]		
		1 day	14 day	28 day
LZnO	Wollastonite	58	74	87
	Talc	62	76	79
	Phosphate Ca	55	63	69
	Phosphate Mg/Ca	68	78	78
	Phosphate Si/Al/Ca	71	77	85
L0	Wollastonite	60	67	67
	Talc	61	66	70
	Phosphate Ca	51	59	65
	Phosphate Mg/Ca	56	59	63
	Phosphate Si/Al/Ca	69	74	81
AX1	Phosphate Ca	54	59	59

4.3 Flash corrosion evaluation for the anticorrosion paints

Flash corrosion was evaluated for the paints as described in ASTM D 610-85 (Table 5). Flash corrosion was detected for all of the binders (LZnO, L0, AX1). The results for all binders containing an anticorrosive pigment based on the mixture of $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Mg}_3(\text{PO}_4)_2$ are shown in Fig. 4. The best results were obtained with the paints containing the silicate-based pigment (wollastonite), namely 10% for LZnO and 16% for L0. We presume that this was primarily due to the higher pH of wollastonite (pH 10) compared to the remaining pigments (pH 6-8). This is also the reason for the lower flash corrosion observed with the binder LZnO (higher pH after ammonia evaporation than for L0 or AX1). The effect of pH on flash corrosion has been described.⁴² Only with the binder L0 with talc and calcium phosphate was the flash corrosion 50%. Flash corrosion decreased by about two points on the ASTM D 610-85 scale after adding a flash corrosion inhibitor (FCI), shifting the pH to the alkaline region. The effect of NPsZnO in the binder on flash corrosion suppression was not very marked (a decrease of no more than one or two points), which implies that the effect of the cathode reaction (occurring due to the reaction of the Zn^{2+} ions, which might create a layer of hybrid hydroxides with steel-corroding cations) plays a minor role.⁴³

Table 5 Values of flash rust of anticorrosive coatings – ASTM D 610

Binder	Anticorrosive pigment	Flash rust [%]	
		without FCI	with 0.5 % FCI
LZnO	Wollastonite	10	3
	Talc	33	16
	Phosphate Ca	33	10
	Phosphate Mg/Ca	16	3
	Phosphate Si/Al/Ca	33	10
L0	Wollastonite	16	10
	Talc	50	33
	Phosphate Ca	50	10
	Phosphate Mg/Ca	33	16
	Phosphate Si/Al/Ca	33	16
AX1	Phosphate Ca	33	10

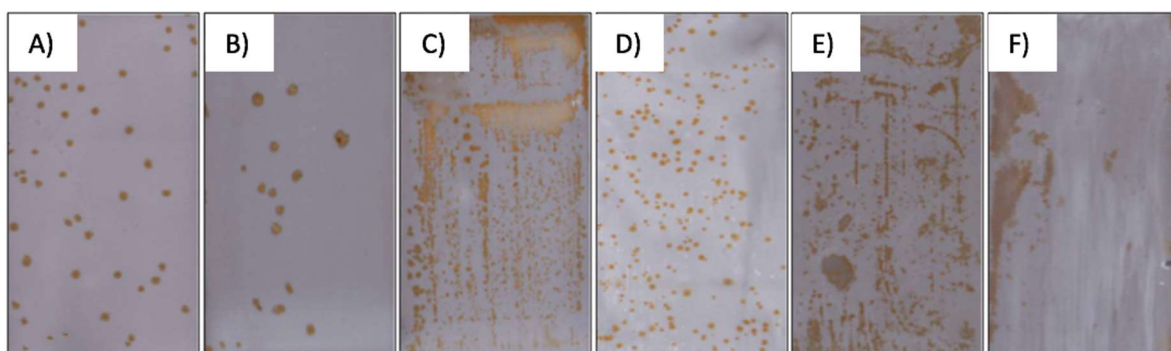


Figure 4 Coating films after the flash rust test (samples containing pigment phosphate Mg/Ca):
 A) LZnO B) LZnO + 0.5% FCI C) L0 D) L0 + 0.5% FCI E) AX1 F) AX1 + 0.5% FCI

4.4 Evaluation of mechanical and chemical resistance of the anticorrosion paints

Mechanical tests and chemical resistance tests were performed as described in the applicable standards. The results are listed in Table 6. The resistance was fairly good for all the paints containing the synthesised binders (LZnO, L0). The best results were obtained in the bend test: none of the film layers suffered damage when bent around the mandrel 4 mm in diameter. The results of the adhesion test by the cross-cut method (knife spacing 1 mm) were also good: any defects were slight only, not exceeding 15%, which led to a score of 2 at the most. Film resistance to the impact of a weight dropping on either side was also measured. The obverse film side resisted excellently (95-100 cm). The values were appreciably poorer when the weight was allowed to impact on the reverse side, e.g. 35-45 cm for the binder LZnO. The reference binder AX1 also exhibited a high resistance to the impact of the weight: its resistance to the weight impact on the reverse side (50 cm) was superior to that of the binders L0 (40 cm) and LZnO (45 cm). On the other hand, the score of the AX1 binder in the adhesion test was 3, and the film was resistant to bending around a mandrel 6 mm but not 4 mm in diameter.

In the MEK test, all the paints with the binder LZnO attained the highest possible levels (resistance against MEK >300 s) as compared to the reference binders (mean resistance against MEK = 25 s). We suggest that the high chemical resistance of the binder with NPsZnO is related to the existence of ionic bonds between the Zn^{2+} cations and the carboxylic groups on the polymeric chains.³⁰ Therefore, the combination of covalent keto-hydrazide and ionic inter-particle crosslinking strategies was shown to be highly advantageous for providing improved mechanical properties and chemical resistance to the resulting coatings.

Table 6 Mechanical resistance of anticorrosive coatings (DFT= $50 \pm 10 \mu m$)

Binder	Anticorrosion pigment	Cupping test [mm]	Falling-weight test - obverse [cm]	Falling-weight test - reverse [cm]	Bend test [mm]	Cross-cut test [-]
LZnO	Wollastonite	9.67	100	40	<4	1
	Talc	> 10	95	35	<4	1
	Phosphate Ca	9.71	100	40	<	1
	Phosphate Mg/Ca	> 10	100	45	4	0
	Phosphate Si/Al/Ca	> 10	100	35	4	0
L0	Wollastonite	8.96	95	35	4	2
	Talc	9.37	95	25	4	1

	Phosphate Ca	9.12	95	20	4	2
	Phosphate Mg/Ca	> 10	100	40	4	1
	Phosphate Si/Al/Ca	> 10	95	40	4	0
AX1	Phosphate Ca	> 10	100	50	6	3

The highest mechanical resistance was observed for the paint with the Mg/Ca phosphate pigment. Very high mechanical resistance levels were also obtained with Si/Al/Ca phosphates and with wollastonite, acting by the barrier mechanism and reinforcing the paint film owing to its specific particle size.

4.5 Evaluation of the corrosion resistance of the paint films after exposure to a condensation-water atmosphere

The paint films were exposed to a condensation-water atmosphere for 480 hours; the results are provided in Table 7. No corrosion was found around the test cut made in the paints when using the binders L0 or LZnO. Blistering, however, was appreciable. The high water absorption by the films was presumably due to the presence of polar hydrazide and carbonyl groups in the polymeric chain. The blister size was 6-8 for all films; the intensity was moderate (M), moderately dense (MD) and dense (D). Film surface defects caused by substrate metal corrosion were minimal; the values were from 0.01% to 10%. The highest anticorrosion efficiency (score 62) was exhibited by the paint with the binder LZnO and the pigment based on aluminium phosphate, silicon oxide and calcium oxide.

Table 7 Results of anti-corrosion efficiency after 480 hours in a condensation-water atmosphere.

Binder	Anticorrosion pigment	Corrosion in cut [mm]	Corrosion of metal substrate [%]	Osmotic blisters of paint film [-]	Rusting on surface paint film [%]	Calculated anticorrosion efficiency [-]
	Wollastonite	0	50	8M	3	56
	Talc	0	50	6MD	0,01	53
LZnO	Phosphate Ca	0	16	6M	10	58
	Phosphate Mg/Ca	0	50	6MD	3	51
	Phosphate Si/Al/Ca	0	50	8M	0,01	62
	Wollastonite	0	50	8D	3	46
	Talc	0	100	8D	10	47
L0	Phosphate Ca	0	33	8M	10	57
	Phosphate Mg/Ca	0	50	8MD	3	50
	Phosphate Si/Al/Ca	0	50	6M	1	57
AX1	Phosphate Ca	0,3	33	4M	33	43

4.6 Evaluation of the antimicrobial resistance of the paints designed for mineral substrates

The antibacterial effect of ZnO is manifested primarily in its nanostructural form.⁴⁴ In general, the antimicrobial action of nanomaterials is attributed to their high specific surface area and their characteristic physical-chemical properties. However, the exact mechanisms of NPsZnO action have not been fully understood yet and are the subject of many discussions.⁴⁵ The following mechanisms are most often predicted: destruction of bacterial cell wall integrity by direct contact with NPsZnO⁴⁶⁻⁴⁸, penetration of soluble toxic ions (mainly Zn²⁺) into cells as well as the formation of reactive oxygen

molecules, hydroxyl radicals and peroxides (the main factor is reactive oxygen that damages the cell wall).⁴⁹⁻⁵² Collection cultures of *Staphylococcus aureus* (CCM 4223), *Escherichia coli* (CCM 4517), *Pseudomonas aeruginosa* (CCM 3955), *Penicillium chrysogenum* (CCM 8034) and *Aspergillus brasiliensis* (CCM 8222) were used for these tests. The samples were used on their own (no biocide) and with the addition of 0.1 and 0.3 wt.% (based on total paint formulation) zinc omadine biocide.

The dependence of the antimicrobial efficiency against bacteria on the antimicrobial additive content is shown in Fig. 5. The binder LZnO without the biocide exhibited the highest antimicrobial efficiency against all bacteria, up to 95% ± 5%, while the mean efficiency of the reference binder L0 was only 50% ± 10%. The efficiency of the binder LZnO increased to 100% for all bacteria after adding 0.1 wt.% zinc omadine. The efficiency of the binder L0 was 95% against *E. coli* and *S. aureus* and 90% against *P. aeruginosa* after adding 0.1 wt.% zinc omadine. The efficiency both of the binders was 100% after adding 0.3 wt.% zinc omadine.

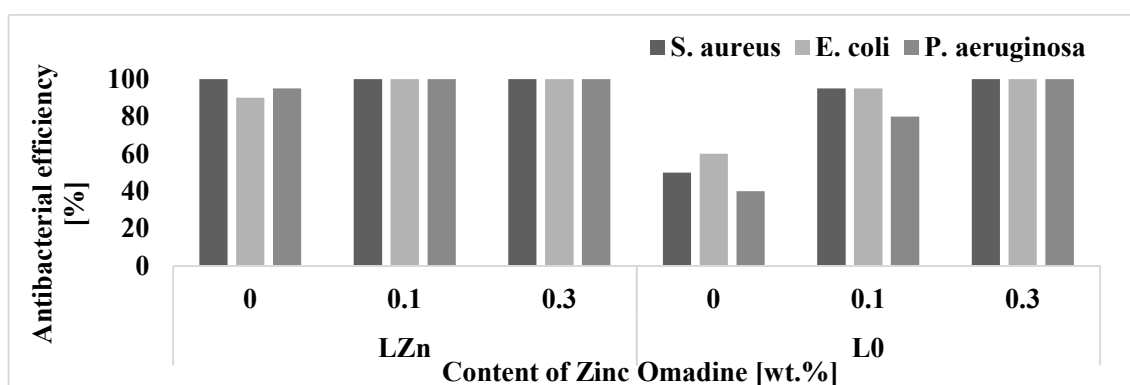


Figure 5 The dependence of antibacterial efficiency on an antimicrobial additive

The dependence of the fungicidal efficiency on the antimicrobial additive content is shown in Fig. 6. The resistance against moulds of the binder LZnO with no inhibitor was high (95% to 100%) and no appreciable inhibition zone was created around the sample. The efficiency increased to 100% for all samples upon the addition of 0.1 wt.% and 0.3 wt.% inhibitor; however, large inhibition zones, which are undesirable in this case, were formed, showing that the biocide is released into the environment, which is an environmentally adverse effect.

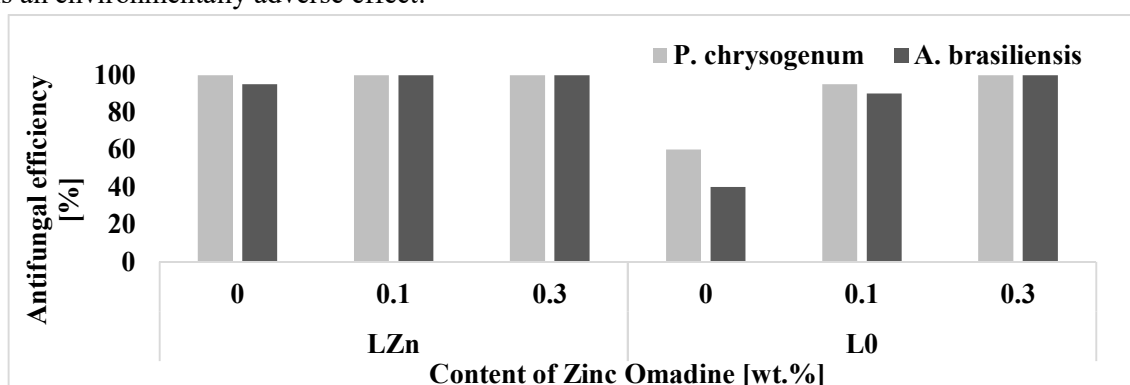


Figure 6 The dependence of antifungal efficiency on an antimicrobial additive

The results shown in in Figs. 5-7 give evidence that if a binder containing ZnO nanoparticles is combined with a suitable pigment, the amount of organic or other biocides added to the paint system can be reduced or eliminated altogether. Note: the antimicrobial properties of the commercial binder were not examined because its composition is unknown, i.e. we do not know which biocides are present and in which amounts.

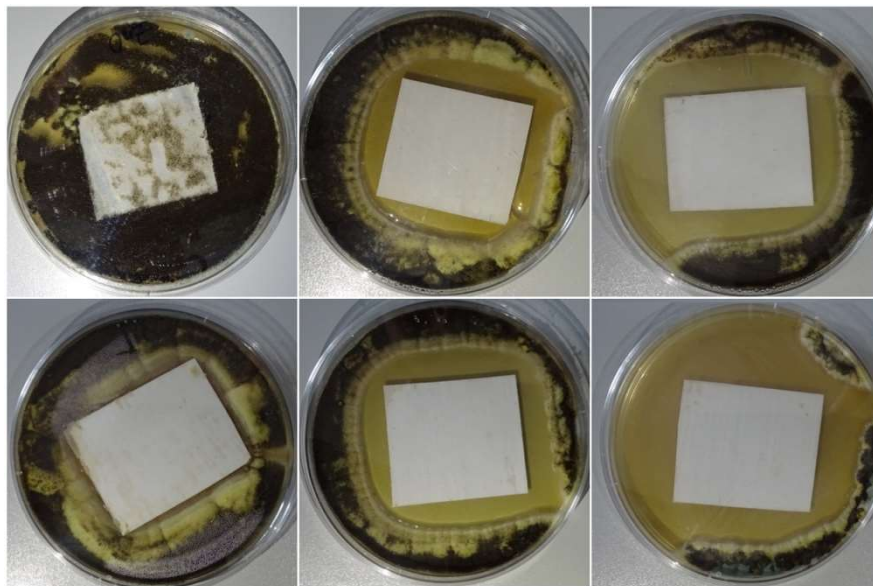


Figure 7 Fungicidal efficiency against *A. brasiliensis* of interior paints containing binder LZnO (upper) and binder L0 (lower); 0 wt.% ZO (left); 0.1 wt.% ZO (centre); 0.3 wt.% ZO (right)

Conclusions

The aim of this work was to examine the properties of new self-crosslinking latexes with incorporated NPsZnO as binders for paints whose films exhibit enhanced chemical, anticorrosion and antimicrobial resistance. The incorporation of NPsZnO was achieved during latex synthesis performed by the two-step emulsion polymerisation technique. The binder with 0.52 wt.% NPsZnO possessed overall better use properties than the laboratory-prepared binder with no nanoparticles and was also better than another commercial water-based binder. The binder with NPsZnO exhibited resistance to MEK up to ~90% higher than the reference binders. Films containing the NPsZnO binder showed generally better mechanical properties, particularly with regard to adhesion (by as much as 3° compared to the commercial binder). Anticorrosion pigments exhibited active chemical and electrochemical effects (pigmented with calcium aluminium polyphosphate silicate hydrate, calcium magnesium orthophosphate and calcium hydrogen phosphate); the binder containing NPsZnO showed promising properties for use in waterborne anticorrosion paints applicable to metallic substrates for environments with a moderate corrosion burden. A combination of latex with a pigment based on a mixture of calcium aluminium polyphosphate silicate hydrate appeared to be the best of the systems tested with respect to long-term corrosion protection owing to the enhanced phosphate group content and a potential synergistic effect of the Al³⁺ and Ca²⁺ cations with the Zn²⁺ cations present in the LZnO binder. The anticorrosion parameters were roughly 5% to 10% poorer if pigments acting on the barrier principle (wollastonite and talc) were used. On the other hand, paints with wollastonite as the pigment based on either synthesised binder exhibited the lowest flash corrosion of the steel substrate; owing to the high pH, flash corrosion was formed on 10-16% of the steel substrate, while values generally between 33% and 50% were observed when the other pigments with a lower pH (6-8) were used (all data without FCI addition). The antimicrobial interior paints containing the binder with incorporated

NPsZnO exhibited an antimicrobial efficiency $45\% \pm 10\%$ higher than that of the paint based on the comparative laboratory-prepared binder without nanoparticles, thereby providing evidence of the antibacterial and antifungal effect of NPsZnO. This will permit the amounts of organic biocidal additives to be reduced by as much as one third.

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