

UNIVERSITY OF PARDUBICE

FACULTY OF CHEMICAL TECHNOLOGY

Institute of Chemical and Technology of Macromolecular Materials

Denisa Steinerová

**Organic environmentally friendly coatings for the surface
protection of metallic and non-metallic materials based on acrylic
latexes with nanoparticles MeO**

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Author: **Ing. Denisa Steinerová**

Supervisor: **prof. Ing. Andréa Kalendová, Dr.**

Supervisor specialist: **prof. Ing. Petr Humpolíček, Ph.D.**

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Abstract

Thesis deals with the simple preparation of environmentally friendly acrylate latex binders functionalized with nanoparticles of metal oxides, namely MgO, ZnO, La₂O₃ and combinations of MgO and ZnO. Nanoparticles were used as functional components providing not only the antimicrobial properties but also improving the physico-mechanical properties and chemical resilience. Latexes containing the 0.5–1.3 % nanoparticles relative to the polymer content were fabricated by the using of the two-stage semi-continuous emulsion radical polymerization technique. The uncoated powder nanoparticles were used. Impact of both the type and concentration of metal oxide nanoparticles in latex were studied in context of their properties. The results showed that all types of nanoparticles provide a very promising properties to latex. The effect was concentration dependent. The nanoparticles in latex provided interfacially crosslinked transparent smooth coating films with high gloss and good physico-mechanical properties. Latexes containing the highest concentration of nanoparticles provided coatings with significant antimicrobial activity against all tested bacterial and fungal strains. Moreover, the InCan antimicrobial stability of liquid latex were improved. Furthermore, the coatings were resistant to solvents, and in addition, latexes with MgO nanoparticles showed a significant decrease in the minimum film-forming temperature. Remarkably, the latex with a concentration of about 1.3% MgO did not show any flash corrosion under the coating film cast on a steel substrate. The latexes containing MgO and La₂O₃ nanoparticles provided coatings resistant to water bleaching. Anti-corrosion coatings prepared from latexes with the highest concentration of nanoparticles provided evidence that cross-linking due to nanoparticles has a beneficial effect on anti-corrosion properties, especially against humid atmospheres. Furthermore, due to pigmentation, there was no deterioration of antibacterial activity and only a slight decrease in antifungal activity.

Keywords

self-crosslinking acrylic latex, ionic crosslinking, metal oxide nanoparticle, antimicrobial activity, anticorrosion activity

Abstrakt

Disertační práce se zabývá jednoduchou přípravou ekologicky přijatelných akrylátových latexových pojiv, které jsou funkcionalizovány nanočásticemi oxidů kovů, konkrétně MgO, ZnO, La₂O₃ a kombinací MgO a ZnO, sloužících jako funkční složky pro dosažení antimikrobiálních vlastností, ale také pro zlepšení fyzikálně-mechanických vlastností a chemické odolnosti. Začlenění práškových nanočástic bez povrchové úpravy bylo provedeno v průběhu syntézy, a to technikou dvoustupňové emulzní polymerace, čímž byly získány latexy obsahující 0.5–1.3 % nanočástic vzhledem k obsahu polymeru. Změny užitečných vlastností latexů vlivem nanočástic byly studovány z hlediska typu a koncentrace nanočástic oxidů kovů v latexu. Výsledky testů ukázaly, že všechny typy nanočástic vykazovali velmi slibné vlastnosti, přičemž se zvyšující se koncentrací nanočástic docházelo ke zlepšování vlastností. Nanočástice v latexu poskytly mezifázově zesítené transparentní hladké nátěrové filmy s vysokým leskem a dobrými fyzikálně-mechanickými vlastnostmi. Latexy obsahující nejvyšší koncentraci nanočástic poskytly nátěry s výraznou antimikrobiální aktivitou vůči všem testovaným bakteriálním a plísňovým kmenům, ale také antimikrobiální stabilitu tekutého latexu, tzv. InCan stabilita. Dále byly nátěry odolné vůči rozpouštědlům, a navíc latexy s nanočásticemi MgO vykazovaly výrazný pokles minimální filmotvorné teploty. Latex s koncentrací 1.3 % MgO nevykazoval bleskovou korozi pod nátěrem naneseným na ocelový podklad. Latexy obsahující nanočástice MgO a La₂O₃ poskytovali povlaky, které byly velice odolné vůči bělení vodou. Antikorozi nátěrové hmoty připravené z latexů s nejvyšší koncentrací nanočástic poskytly důkaz, že zesítení vlivem nanočástic má příznivý vliv na antikorozi vlastnosti, a to především vůči atmosférám s vysokou relativní vlhkostí. Dále vlivem pigmentace nedošlo ke zhoršení antibakteriální aktivity a pouze k mírnému snížení antifungální aktivity.

Klíčová slova

Samo-sítující akrylový latex, iontové síťování, nanočástice oxidu kovu, antimikrobiální aktivita, antikorozi aktivita

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1. Introduction

Great efforts are currently being made to use environmentally friendly coatings [1,2], but at the same time, there is a growing demand for antimicrobial coatings worldwide [3,4], as evidenced by a large number of articles and patents. Combining these two requirements is not an easy task, as one of the biggest trends in the market for green coatings is the introduction of low or zero volatile organic solvent (VOC) technologies, leading to the use of waterborne or solvent-free coatings. Waterborne coatings are an excellent alternative to solvent-based coatings, as they are a universal, high-quality, and environmentally friendly choice that meets both European (BPD – Biocidal Products Directive) and US (EPA – Environmental Protection Agency) regulations that require VOCs to be below 350 g/L water [5]. However, a serious drawback of waterborne coatings is that they are subject to microbial colonization, both during storage and later as a coated film [6]. This leads to the use of biocidal substances, and although there is a wide choice of biocidal additives for paints and coatings, they are often toxic or even carcinogenic substances [7] and thus environmentally unacceptable, and therefore environmentally unacceptable, and they are becoming increasingly restricted.

Acrylate latex paints are probably the most widely used commercially produced polymeric colloids [5,8], mainly due to their easy preparation and modification. In addition, they are characterized by low toxicity, high resistance to atmospheric conditions, fast drying at room temperature, and compatibility with a wide range of surfaces, such as metals, plastics, or wood. An equally important advantage is good usability for the target customer, thanks to easy washing with water (before curing) and low odor. Due to these properties, they have become very popular despite their typical shortcomings, such as the formation of flash corrosion, and low resistance to high and low temperatures or solvents and water, which often limits their applicability [9].

One way to improve the durability of latex coatings is to crosslink polymer chains with covalent or ionic bonds [10]. Researchers have developed a number of crosslinking mechanisms for latex films [11,12], both two-pack and one-pack (self-crosslinking) compositions, with "two-pack in one pot" systems. The one-pack compositions are preferred, mainly for ease of use. In these systems, the crosslinking reaction is usually triggered either by a drastic decrease in pH or by evaporation of water during film drying [13]. A particularly effective crosslinking mechanism used in the "two-pack in one pot" latex compositions is based on a reaction between carbonyl groups in diacetone acrylamide repeat units (DAAM), which are part of the polymer chain, and hydrazide groups from adipic acid dihydrazide (ADH) dissolved in the aqueous phase [14,15]. The unique feature of this reaction is rapid curing at room temperature which further increases the barrier properties, mechanical properties, and water-repellent properties of coating films [15].

As already mentioned, waterborne paints are sensitive to biodegradation by bacteria and fungi while in the can, or later as an applied coating film. Various inorganic and organic materials have been used for this purpose in the past, but many of them are now banned due to their harmfulness to human health or the environment and thus non-compliance with relevant European legislation (the European Union specifically adopted Directive 98/8/ES). Current findings stimulate further reductions in the number of substances with antimicrobial effects. Therefore, new environmentally friendly

alternatives to antimicrobial protection should be sought [16], as microbial infectious diseases are serious health and socio-economic problem which attracts the attention of the public around the world [17].

Nanoparticles provide a new approach to the development of antimicrobial materials. In particular, metal oxide (MeO) nanoparticles have the potential to be effective against a wide range of microorganisms (MO), such as aerobic bacteria, anaerobic bacteria, viruses, yeasts, and fungi [3,18]. Metal cations are thought to destroy the enzymes of these MOs and are therefore unable to build up a resistance [19]. Although the mechanism of action is not yet fully understood, metal cations are reported to interact with proteins by attaching to a thiol group, thereby inactivating the proteins [20]. It is further hypothesized that when metal cations enter a bacterial cell, the DNA molecule changes to a condensed form and loses its ability to replicate, leading to cell death [21,22]. An example of a promising MeO with an antimicrobial effect is nanostructured La_2O_3 which has been found to inhibit the growth of bacteria, fungi, and yeast and for this reason, it was investigated in safety and biomedical applications [23].

In addition to antimicrobial properties, MeO nanoparticles can also have a positive effect on the structural properties of the coating [24,25]. If limited soluble MeO nanoparticles are used, the properties of acrylate latex coatings can also be improved by ionic (physical) crosslinking with subsequent complex formation, which occurs in the interfacial zones between adjacent latex particles, through ionic dipolar interactions [10]. In the case of carboxy-functionalized latexes, ionic bonds are formed between carboxyl groups on the surface of latex particles in the presence of polyvalent metals or metal complexes [26,27]. ZnO (often reported in the relevant literature) appears to be a suitable crosslinker, as it is a sparingly soluble metal oxide that does not dramatically affect latex stability [28]. Ammonia, which is often used to ensure the stability of the latex system, reacts with zinc ions to form a zinc amine complex. Upon evaporation of ammonia and water in the film-forming process, zinc ions are released from the complex and react with the carboxyl groups on the surface of the latex particles at room temperature. The ionic crosslinking reaction is first formed between zinc ions and carboxyl groups and then transformed into a more thermodynamically stable coordinated complex. Compared to conventional latexes, these compositions offer excellent thermal stability, hardness, resistance to water, weathering, etc. [29].

The problem of flash corrosion of latex coatings limits their use on metal substrates (especially steel), where the soluble iron salt is transferred to the coating film during drying [30]. In practice, this problem is solved using often toxic flash corrosion inhibitors, such as sodium benzoate or sodium nitrite [31,32]. The corrosion potential of the metal and the nature of corrosion are mainly dependent on the concentration of hydrogen ions in the aqueous medium (pH). Pourbaix diagrams can be used to predict the corrosion behavior of a metal substrate [33]. In the case of a steel substrate according to the Pourbaix diagram for iron, it can be expected that at pH above 8.5 the steel passes into the passivity region and no iron oxidation occurs. Thus, the solution to this problem could be to alkalize the latex with an agent that will not leak during the drying process and will maintain a high pH (above 8.5) throughout the coating process. MgO appears to be a suitable candidate which dissociates into hydroxyl and magnesium ions in an aqueous medium, thus shifting the pH of the aqueous solution to the alkaline range [34,35].

2. Aim of theses

The aim of the presented dissertation is the synthesis of environmentally safe self-crosslinking acrylate latexes with MeO nanoparticles at different concentrations and the characterization of their basic properties, especially the antimicrobial efficiency, imparted to the latex by the nanoparticles, in comparison with the acrylate latex without the relevant nanoparticles synthesized by the same procedure. The goal of the work is also to determine whether the cross-linking chemistry will improve the otherwise low anti-corrosion efficiency of acrylic paint films.

The objectives of the dissertation can be clearly summarized in the following points:

- 1. Synthesis and characterization of acrylate latexes with different types and concentrations of inorganic nanoparticles** (namely MgO, ZnO, La₂O₃ and combinations of MgO and ZnO).
 - Synthesis of four series of acrylate latexes by the technique of semi-continuous emulsion radical polymerization, differing in the type and content of inorganic nanoparticles (specifically MgO, ZnO and La₂O₃ with a concentration of 0.5, 1 and 1.5 wt.% and a combination of MgO and ZnO nanoparticles, where MgO was always supplied at a concentration of 1 wt.% and ZnO at a concentration of 0.25, 0.5 and 0.75 wt.%) and a comparison latex without the respective nanoparticles.
 - Basic characterization of acrylate latexes and determination of the effectiveness of incorporation of inorganic nanoparticles into the colloidal system of latexes.
 - Study of the effect of inorganic nanoparticles on the physical-mechanical, chemical and flash corrosion resistance of paint films using standardized tests.
 - Determining the degree of cross-linking introduced into the latex by keto-carboxyl chemistry and embedded inorganic nanoparticles.
 - Study of the influence of inorganic nanoparticles on antibacterial efficiency using the modified ISO 22196 standard.
 - Selection of the most successful representative from each prepared series of acrylate latexes and carrying out a more detailed study.

- 2. Preparation and study of anti-corrosion coatings based on the most successful representative from each prepared series of acrylate latexes** (L_{MgO-1.5%}, L_{ZnO-1.5%}, L_{La2O3-1.5%}, L_{MgO+ZnO-1.75%}).
 - Formulation of pigmented model anti-corrosion coatings.
 - Study of the influence of nanoparticles and OKP on the physical-mechanical and chemical resistance of paint films using standardized tests.
 - Study of the influence of nanoparticles and OKP on the corrosion resistance of paint films using corrosion tests and electrochemical techniques.
 - Study of the effect of pigmentation on antibacterial efficiency using the modified ISO 22196 standard and antifungal efficiency using the modified ASTM D5590 standard.

3. Experimental Part

3.1. Synthesis of latexes

Using the technique of semi-continuous emulsion radical polymerization, four series of acrylate latexes were prepared, which differed in the type and content of inorganic nanoparticles. To allow interparticle crosslinking, DAAM providing ketone carbonyl functional groups for subsequent crosslinking with a hydrazide crosslinking agent was added to the polymer chain. DAAM and nanoparticles were delivered to the system only in the second phase of the monomer drip. The ratio composition of the monomers making up all the latexes was: 86 g MMA, 106 g BA, and 8 g MAA dosed in the first phase and 78 g MMA, 104 g BA, 8 g MAA, and 10 g DAAM dosed in the second phase. The ratio of acrylate monomers forming latex particles was chosen so that the calculated glass transition temperature (T_g) of the latex polymer was around 10 °C (calculated according to Fox's equation [36]) to ensure sufficient film formation and non-stick coatings. The L_0 latex sample was a reference without the corresponding inorganic nanoparticles, while the L_{ZnO} samples contained ZnO nanoparticles, the L_{MgO} samples contained MgO nanoparticles and the $L_{La_2O_3}$ samples contained La_2O_3 nanoparticles, each with a concentration of 0.5, 1, and 1.5 wt. % (based on the total amount of monomers). The last series of $L_{MgO+ZnO}$ acrylate latexes combined MgO and ZnO nanoparticles, with MgO nanoparticles each being supplied with a concentration of 1 wt. % and ZnO nanoparticles in a concentration of 0.25, 0.5 and 0.75 wt. % (based on the total amount of monomers).

After synthesis, the solids were filtered to calculate the coagulate content, the pH of the cold latex was adjusted to 8.5 with 10% aqueous ammonia (for latexes having an initial pH below 8.5), and finally a 10% aqueous solution of ADH was added in an amount corresponding to a molar ratio of DAAM : ADH = 2 : 1, whereby the self-crosslinking latex binders were prepared.

3.2. Characterization of latexes

The coagulate and coarse impurity contents of the latexes were determined by sieve analysis according to ČSN 64 9008; pH was measured with a Mettler Toledo FiveEasy FE20 pH-meter (Merck KGaA, Darmstadt, Germany) [37]; the minimum film-forming temperature (MFFT) was determined by using a MFFT-60 instrument (Rhopoint Instruments, East Sussex, UK) according to ISO 2115; the storage stability of latexes was tested in two storing modes: 1. at 50 °C for 2 months; 2. at 25 °C for 2 years. The evaluation was performed using the zeta potential and the particle size by the dynamic light scattering (DLS) method on a Zetasizer Nano ZS (Malvern Panalytical, Malvern, UK) [38]; the InCan antimicrobial efficiency of the liquid latexes was tested by using Preventol® Dipslides (LANXESS Deutschland GmbH, Cologne, Germany). The InCan Preservation test of antimicrobial efficiency consisted of submerging the agar part of the DipSlide into the latex for 10 s, followed by incubation at 30 °C for 120 h. The result was evaluated by using standards [39].

3.3. Coating film property assessment

Determination of real nanoparticle content in coating films of acrylate latexes was performed by using of an inductively coupled plasma optical emission spectrometry (ICP-OES) using an Integra 6000 (GBC Scientific Equipment, Braeside, Australia) [40]. From the values obtained, the nanoparticle content was calculated using the simplified assumption that all nanoparticles are in the coating film only in the form of the respective metal oxide. (except for La_2O_3 -based, where $\text{La}_2\text{O}_2\text{CO}_3$ was considered according to XRD analysis results).

The degree of crosslinking of acrylate latexes was evaluated based on gel content and crosslink density. The gel content was determined according to ČSN EN ISO 6427 by extraction in a Soxhlet extractor with tetrahydrofuran for 24 hours. Crosslinking density was performed by swelling loose films of acrylate latexes in toluene at 35°C for 7 days and employing the theory of Flory and Rehner [41], were used to calculate the crosslink density.

The optical properties of coating films were evaluated with respect to gloss, transparency and water whitening. The gloss was evaluated according to ČSN EN ISO 2813, the transparency and water whitening of coating films were evaluated by light transmission (transmittance measurement at a wavelength of 500 nm) using a ColorQuest XE Spectrometer (Hunterlab, VA, US).

The hardness of the coating films was evaluated according to ČSN EN ISO 1522 – Paints and varnishes – Pendulum damping test; Persoz type pendulum (3034M001 pendulum, Elcometer Instruments GmbH, Aalen, Germany). The mechanical properties (mechanical resistance) of the coating films were assessed according to ČSN EN ISO 6272-2 – Paints and varnishes – Rapid-deformation (impact resistance) test using an Elcometer 1615 variable impact tester (Elcometer Instruments GmbH, Aalen, Germany). Tests according to ČSN ISO 2409, the cross-cut test, were also made. An Elcometer cross-cut system (Elcometer Instruments GmbH, Aalen, Germany) with 6 parallel knives 1 mm apart was used. Chemical resistance of the coating films was assessed according to ASTM D-4752-10 – rubbing test with methyl ethyl ketone (MEK). Flash corrosion resistance of the coating films was assessed through a laboratory test to identify any flash corrosion [32]. The corrosion phenomena were scored as per ASTM D 610-85; coloration was scored using Gardner's iodometric scale.

The antimicrobial efficiency of the coating films was evaluated using a modified method ISO 22196 [42] to determine the antibacterial activity. Four bacterial strains were used for antimicrobial tests, namely *Staphylococcus aureus* (*S. aureus*, CCM 4516), *Escherichia coli* (*E. coli*, CCM 4517), *Enterococcus faecalis* (*E. faecalis*, CCM 3956) and *Klebsiella pneumoniae* (*K. pneumoniae*, CCM 4425). The testing of antibacterial activity was performed on sterile loose films with dimensions of 25 × 25 mm² which were inoculated with 0.1 mL of a specific standardized bacterial suspension (24-hour culture). The inoculated samples were then covered with a sterile polypropylene film and incubated at 35 °C for 24 hours at 95% RH. After incubation, the polypropylene film was removed, and each sample was imprinted on three different agar areas and incubated at 35 °C for 24 hours. The results were then evaluated from 0 to 5, with 0 representing the best antibacterial activity, i.e., without the growth of bacterial colonies.

3.4. Paint formulation and preparation

For the preparation of model anti-corrosion coatings, HEUCOPHOS® ZP-10 was chosen as an anti-corrosion pigment, a pigment with medium anti-corrosion efficiency, as well as Plastorit® Micro to increase the adhesion of the resulting coating film to the substrate and Hematite Bayferrox 130 M as a filler. Formulation of model paint materials was carried out in the "FORMUL" program. The most successful synthesized acrylate binders with the highest concentration of MeO nanoparticles and an acrylic resin without nanoparticles as a reference were used for the preparation of anti-corrosion coatings. Dispersion was carried out using highly concentrated pigment aqueous pastes. The investigated acrylate latexes were prepared at a pigment volume concentration (PVC) of 3, 5 and 10% of HEUCOPHOS® ZP-10 pigment. Plastorit® Micro was added to increase the PVC by 2% and the pigment system parameter was adjusted to $Q = 45\%$ using Hematite Bayferrox 130 M filler. To achieve the desired properties, additives were added to the formulation so that it did not exceed 1 wt. % of the total amount of paint. Prepared organic coatings were applied to steel and glass panels using an applicator with a slit. Subsequently dry film thickness was determined using magnetic gauge.

3.5. Corrosion resistance of anti-corrosion coatings

The determination of the corrosion resistance of organic coatings was carried out according to the ČSN 03 8131 – Corrosion test in a condensation chamber, carried out in a KB 400 MA-TR-K chamber (Gebr. Liebisch, Germany) with 100% air humidity and a temperature of 38 ± 2 °C and according to the ČSN ISO 9227 – Corrosion test in artificial atmospheres – Salt mist test, using a salt box chamber SKB400ATR (Gebr. Liebisch, Germany), which stimulates an environment with an increased chloride content – 5% NaCl mist with increased air humidity and a temperature of 35 ± 1 °C.

The evaluation was carried out according to: The degree of blistering on the surface of the coatings (ASTM D 714-78), the degree of corrosion at the test scribe (ASTM D 1654-92) and the degree of steel surface corrosion (ASTM D 610-85) were evaluated after the exposure in the corrosive environments.

4. Result and discussion

4.1. Properties of latexes

Characteristic properties of all prepared liquid latexes are given in Tab. 1. As can be seen from the results, the resulting properties of the latexes were affected by both the type of added nanoparticles and their concentration. It was found for all series of latexes that the coagulum content increased with the increasing content of incorporated inorganic nanoparticles. From this it can be concluded that the presence of nanostructured MeO caused a slight decrease in the colloidal stability of the dispersion during synthesis, probably due to the hydration reaction of the respective metal oxide to form water-insoluble relevant hydroxide and dissociated OH^- and Me^{x+} ions, which resulted in increased ionic strength of the dispersion medium, i.e. agglomeration of latex particles. The presence of dissociated ions (probably in a low concentration, but not negligible) is also evidenced by the increased pH value, which again increased with the increasing concentration of nanoparticles. When comparing the types of nanoparticles, the pH value is the highest in the case of latexes containing MgO nanoparticles, which corresponds to their solubility in water compared to nanoparticles ZnO and La_2O_3 (solubility in water at room temperature: MgO = 86 mg/L, ZnO = 1.6 mg/L and La_2O_3 = 4 mg/L [43]).

Table 1: Characteristics of latexes differing in type and content of embedded nanoparticles

Sample	Theoretical nanoparticle content (wt.%)		Coagulum content (wt.%) ^a	pH ^a	MFFT (°C) ^b	InCan stability ^b	
	Coating film	Liquid binder				Bacteria (cfu/mL)	Fungi (deg.)
L ₀	0	0	0.1	2.12	8.1	1 × 10 ⁶	Heavy
L _{MgO-0.5%}	0.5	0.2	0.3	7.50	3.0	1 × 10 ⁵	Heavy
L _{MgO-1%}	1	0.4	0.5	8.62	2.2	1 × 10 ⁴	Moderate
L _{MgO-1.5%}	1.5	0.6	0.6	10.24	0.5	<1000	None
L _{ZnO-0.5%}	0.5	0.2	0.4	5.53	9.0	<1000	None
L _{ZnO-1%}	1	0.4	0.5	6.00	9.9	<1000	None
L _{ZnO-1.5%}	1.5	0.6	0.8	6.08	11.5	<1000	None
L _{MgO+ZnO-1.25%}	1.25	0.5	1.1	10.12	2.5	<1000	None
L _{MgO+ZnO-1.5%}	1.5	0.6	1.9	9.93	4.8	<1000	None
L _{MgO+ZnO-1.75%}	1.75	0.7	2.8	9.46	6.9	<1000	None
L _{La2O3-0.5%}	0.5	0.2	0.3	5.27	10.7	1 × 10 ⁴	Moderate
L _{La2O3-1%}	1	0.4	0.6	5.71	11.9	1000	Light
L _{La2O3-1.5%}	1.5	0.6	1.0	5.85	14.4	<1000	None

^a Determined before ammonia and ADH addition to the latex

^b Determined after ammonia and ADH addition to the latex

The effect of the type and concentration of embedded nanoparticles on MFFT was also observed, where the results probably indicate two phenomena caused by the presence of nanoparticles, namely interfacial ionic crosslinking owing to the presence of dissociated Me^{x+} ions leading to increased MFFT and hydroplasticization of carboxyl emulsion copolymer leading to decreased MFFT. The first effect was more pronounced in latexes containing ZnO and La_2O_3 nanoparticles, which exhibited increased MFFT with increasing concentration of nanoparticles, i.e. with increasing concentration of

dissociated Me^{x+} ions leading to ion-phase crosslinked film through the reaction between carboxyl groups of emulsion copolymer and metal cations. This led to suppression of mobility and inter-diffusion of the polymer chains, thereby the deformability of the latex particles in the coalescence phase get worse, leading to an increase in MFFT. In contrast, for the latexes with MgO nanoparticles, a second effect causing a decrease in MFFT with increasing nanoparticle concentration was observed more markedly, apparently due to hydroplasticization of the carboxyl emulsion copolymer. The solubility of MgO in the aqueous dispersion medium, causing the pH to increase, as described above, caused a permanent neutralization of a significant amount of carboxyl groups during film formation. The ionized carboxyl groups are responsible for the higher amount of molecularly bound water in the latex copolymer [44,45], which results in softening of the polymer chains throughout the film drying process, leading to a decrease in MFFT even with dense interfacial crosslinking. Significant hydroplasticization of latex particles was also observed in latexes combining MgO and ZnO nanoparticles, which, however, decreased with increasing concentration of ZnO nanoparticles (concentration of incorporated MgO nanoparticles was set constant – theoretically 1wt .% in the coating). This effect was probably due to decreasing the real content of MgO nanoparticles in the latex due to intensified coagulum formation rich in MeO nanoparticles.

The results of InCan testing of aqueous dispersions provided evidence of the antimicrobial efficacy of dispersed MeO nanoparticles. While the reference latex (nanoparticle-free) showed the presence of bacteria at a density of 1×10^6 cfu/mL and high yeast coverage, the latexes with nanoparticles showed suppression of the growth of microorganisms. Based on the results, ZnO nanoparticles, which already showed microbicidal activity at the lowest concentration, appeared to be the most suitable InCan antimicrobial additive. In contrast, MgO and La_2O_3 nanoparticles showed microbicidal activity only at the highest concentration, and at lower concentrations of nanoparticles, there was only a partial suppression of the growth of microorganisms, which increased with increasing nanoparticle concentration. However, a serious disadvantage of ZnO nanoparticles is their toxicity to the aquatic environment [46,47] and mammalian cells [48,49]. It is, therefore, appropriate to decrease the concentration of ZnO nanoparticles as low as possible and look for new alternatives to antimicrobial protection. For this reason, a series of latexes combining ZnO and MgO nanoparticles was also prepared, where antimicrobial protection of the liquid latex occurred at a theoretical concentration of 0.25 and 1 wt.% of ZnO and MgO nanoparticles, respectively. The antimicrobial activity of MeO nanoparticles can be attributed to lipid peroxidation, the formation of reactive oxygen species or the presence of metal cations destroying MO enzymes. However, it should be noted here that the exact mechanism of antimicrobial protection of metal oxide nanoparticles has not yet been fully elucidated. Alkaline latexes may also play a role in their alkalinity, which creates an unfavorable environment for MOs and also increases the activity of reactive oxygen species [49].

In view of the risk of premature destabilization of the latexes already during storage due to the presence of inorganic nanoparticles, testing of the stability of the latexes during storage was performed. Particle size and zeta potential were assessed before storage (the same day of synthesis) and after storage: (i) after 2 months at 50 °C and (ii) after 2 years at RT. The measurement results are shown in Tab. 2. It is clear

from the results that the size of latex particles was significantly affected only in the case of latexes containing MgO nanoparticles, where the particle size was increased with increasing MgO concentration, probably due to the so-called alkali-swelling effect [50]. In the case of zeta potential, the initial values were found to decrease with increasing nanoparticle concentration, which was most pronounced for latexes containing MgO nanoparticles, probably owing to the increased ionic strength of the dispersion medium due to dissolution of the respective MeO. Latexes containing a theoretical concentration of ≥ 1 wt.% of MgO showed values close to -30 mV, indicating an initial risk of instability. Despite this fact, all these latexes have been shown to be stable during storage and resistant to aggregation. After testing, no obvious coagulation, no sedimentation, and no significant changes in the tested properties were observed in any latex. Based on these results, it can be concluded that all latexes can be considered long-term stable.

Table 2: Results of storage stability testing

Sample	Same day of synthesis		After storage test		After 2 years at RT	
	Particle size (nm)	Zeta potential (mV)	Particle size (nm)	Zeta potential (mV)	Particle size (nm)	Zeta potential (mV)
L ₀	125.5 ± 2.0	-39.0 ± 1.7	126.3 ± 3.7	-37.0 ± 1.3	123.7 ± 2.8	-38.2 ± 1.3
LMgO-0.5%	130.5 ± 1.2	-34.7 ± 0.9	131.7 ± 2.6	-34.8 ± 0.5	131.6 ± 2.2	-34.2 ± 1.1
LMgO-1%	152.4 ± 2.6	-28.5 ± 1.4	151.2 ± 1.8	-26.5 ± 1.2	151.6 ± 1.8	-25.0 ± 0.6
LMgO-1.5%	206.8 ± 3.5	-26.8 ± 0.8	205.7 ± 3.6	-25.0 ± 0.7	200.7 ± 3.6	-24.3 ± 0.5
LZnO-0.5%	113.3 ± 1.3	-37.5 ± 0.6	116.1 ± 2.0	-38.9 ± 0.8	115.6 ± 3.9	-41.1 ± 1.1
LZnO-1%	121.9 ± 2.9	-32.4 ± 0.4	122.5 ± 2.0	-36.7 ± 1.1	126.5 ± 1.6	-43.2 ± 1.4
LZnO-1.5%	123.9 ± 2.8	-31.7 ± 0.3	126.1 ± 1.9	-34.5 ± 0.6	128.1 ± 1.4	-45.1 ± 1.1
LMgO+ZnO-1.25%	161.0 ± 3.5	-29.7 ± 1.3	159.4 ± 2.4	-25.1 ± 0.3	162.5 ± 1.6	-25.4 ± 1.2
LMgO+ZnO-1.5%	147.3 ± 2.9	-29.1 ± 1.2	148.8 ± 3.4	-22.9 ± 0.9	152.5 ± 2.9	-23.5 ± 1.0
LMgO+ZnO-1.75%	140.1 ± 1.8	-26.1 ± 1.0	138.7 ± 1.7	-21.5 ± 0.7	141.2 ± 2.4	-23.5 ± 1.0
LLa2O3-0.5%	92.7 ± 0.7	-47.1 ± 1.4	92.1 ± 1.2	-42.4 ± 1.4	92.7 ± 1.1	-44.3 ± 1.5
LLa2O3-1%	117.7 ± 1.4	-43.8 ± 0.8	117.1 ± 0.6	-39.3 ± 1.6	117.8 ± 1.0	-43.3 ± 1.0
LLa2O3-1.5%	119.3 ± 1.7	-39.0 ± 0.8	118.6 ± 1.1	-35.2 ± 1.2	119.0 ± 1.5	-38.0 ± 1.4

4.2. Coating properties of latexes

The content of embedded nanoparticles in coating films was determined using ICP-OES and was used to calculate the real content of nanoparticles in the coating film. The analysis showed that the incorporation efficiency of nanoparticles, both dissolved and stably dispersed in the aqueous latex medium, decreased with increasing content of inorganic nanoparticles incorporated into the latex (see Tab. 3), which also indicates an increase in the proportion of inorganic nanoparticles trapped in the coagulum (see Tab. 1). For this reason, further efforts to increase the content of incorporated nanoparticles seem inefficient.

Table 3: Real nanoparticle content in coating films and aqueous dispersions

Sample	Theoretical concentration of nanoparticles in coating film (wt.%)	Metal concentration (mg/kg)	Real concentration of nanoparticles in coating film (wt.%) ^b	Real concentration of nanoparticles in liquid latex (wt.%) ^c
L ₀	0	0	0	0
Mg				
L _{MgO-0.5%}	0.5	2948 ± 29	0.49	0.20
L _{MgO-1%}	1	5561 ± 23	0.92	0.36
L _{MgO-1.5%}	1.5	7900 ± 41	1.31	0.52
Zn				
L _{ZnO-0.5%}	0.5	3561 ± 34	0.44	0.18
L _{ZnO-1%}	1	7288 ± 47	0.91	0.36
L _{ZnO-1.5%}	1.5	10,618 ± 31	1.32	0.53
Mg + Zn				
L _{MgO+ZnO-1.25%}	1 + 0.25 ^a	5548 ± 41 + 1728 ± 19	0.92 + 0.22	0.37 + 0.09
L _{MgO+ZnO-1.5%}	1 + 0.5 ^a	5478 ± 37 + 3158 ± 27	0.91 + 0.39	0.36 + 0.16
L _{MgO+ZnO-1.75%}	1 + 0.75 ^a	5198 ± 34 + 4209 ± 38	0.86 + 0.52	0.34 + 0.21
La				
L _{La2O3-0.5%}	0.5	3683 ± 26	0.49	0.20
L _{La2O3-1%}	1	7004 ± 35	0.93	0.37
L _{La2O3-1.5%}	1.5	10,580 ± 31	1.41	0.56

^a Latexes combining nanoparticles MgO and ZnO were always prepared using constant amount of MgO (1 wt.% with respect to monomers) and varying amount of ZnO (0.25, 0.5 and 0.75 wt.% with respect to monomers) to achieve the desired concentration.

^b The percentage of inorganic nanoparticles in the dried coating film from the ICP-OES results was calculated using the simplified assumption that the determined metal (Mg and Zn) in the polymer film was only in the form of the corresponding oxide and La was present in the form of dioxycarbonate (as determined by XRD).

^c The percentage of inorganic nanoparticles in the liquid latex was calculated from the actual concentration of nanoparticles in the coating film and the dry matter of the respective latex.

Although MeO nanoparticles were primarily used as antimicrobial additives, their effect on the structural properties of the coating film was also investigated. Nanoparticles of sparingly soluble MeOs have the potential to act as crosslinking agents providing ionic interfacial crosslinking, which significantly affects the properties of the resulting coating film [26]. For this reason, the level of crosslinking was examined from the point of view of the gel content, the average molecular weight between the crosslinking junctions (M_c), and the crosslink density. As can be seen from the results (see Tab. 4), all types of MeO nanoparticles proved to be effective crosslinking agents. Compared to the blank coating (interfacially crosslinked by covalent bonds due to keto-hydrazide reaction), the crosslink density and gel content increased with MeO nanoparticle concentration. When comparing the individual MeO nanoparticles used, it was found that nanoparticulate MgO was the most effective crosslinking agent. This is probably due to its higher solubility, i.e. a higher concentration of dissociated divalent cations and thus an increased amount of neutralized carboxylic acid groups, as discussed above. We further believe that both surface carboxyl groups and those buried inside a latex particle were involved in ionic crosslinking, which provided inter- and intra-particle ionic crosslinks. In this perspective, it can be assumed that substantial intra-particle crosslinking already occurred during the synthesis of the polymer after the delivery of MgO nanoparticles. Furthermore, the measurements showed that La₂O₃ provided coatings of a higher crosslink density than ZnO, which is in good accordance with theoretical solubility values (4.0 and 1.6 mg/L for La₂O₃ and ZnO, respectively). A

trivalent nature of the La cation may also play a role, binding more carboxyl groups than the divalent Zn cation. In the case of latexes combining MgO and ZnO nanoparticles, the degree of crosslinking corresponds to the contribution of the individual MeOs.

Table 4: Effect of the type and concentration of MeO nanoparticles on the degree of crosslinking

Sample	Gel content (%)	M_c (g/mol)	Crosslink density (moles/cm ³)
L ₀	72.7 ± 0.3	76,500 ± 600	1.49 × 10 ⁻⁵
L _{MgO-0.5%}	89.4 ± 0.2	19,500 ± 300	5.74 × 10 ⁻⁵
L _{MgO-1%}	92.1 ± 0.3	14,700 ± 300	7.53 × 10 ⁻⁵
L _{MgO-1.5%}	95.9 ± 0.4	7,900 ± 300	1.40 × 10 ⁻⁴
L _{ZnO-0.5%}	86.0 ± 0.1	29,500 ± 500	3.84 × 10 ⁻⁵
L _{ZnO-1%}	89.9 ± 0.7	22,500 ± 600	5.06 × 10 ⁻⁵
L _{ZnO-1.5%}	91.0 ± 0.5	16,500 ± 100	6.73 × 10 ⁻⁵
L _{MgO+ZnO-1.25%}	92.2 ± 0.5	13,300 ± 400	8.36 × 10 ⁻⁵
L _{MgO+ZnO-1.5%}	95.4 ± 0.4	8,600 ± 200	1.28 × 10 ⁻⁴
L _{MgO+ZnO-1.75%}	96.5 ± 0.6	7,900 ± 400	1.40 × 10 ⁻⁴
L _{La2O3-0.5%}	91.2 ± 0.3	26,200 ± 500	4.43 × 10 ⁻⁵
L _{La2O3-1%}	92.9 ± 0.5	20,500 ± 300	5.44 × 10 ⁻⁵
L _{La2O3-1.5%}	95.3 ± 0.6	12,900 ± 300	8.67 × 10 ⁻⁵

All testing of coating films cast on a substrate (glass or steel) was performed on coatings with a dry thickness of 60 ± 10 μm. The results of optical properties and water whitening are shown in Tab. 5. All prepared coating films were highly transparent and showed high gloss without the presence of defects, regardless of the type or concentration of embedded MeO nanoparticles. Due to the high transparency and gloss of the coating films, it can be assumed that the inorganic nanoparticles in the coating films occurred predominantly at the nanoscale, and during film formation, they did not impair the coalescence of the latex particles [51].

As acrylate latex coatings show wretched water resistance (causing mainly swelling, whitening, and loss of adhesion to a substrate), water whitening testing was also performed, as it is known that water resistance deteriorates with increasing crosslink density [14,52], because water whitening is caused by water domains in the coating film that exceed a certain size (light of longer wavelengths scatters more strongly with increasing domain size). Thus, if the polymer is strongly crosslinked, it contains only small water domains that appear less turbid to the human eye [14]. The measurement results showed in the case of all series of latex films that the level of water whitening decreased with increased MeO nanoparticle concentration and the results of water whitening were in good accordance with the crosslink density results shown in Tab. 4. It was found that latexes containing MgO (including the combination of MgO and ZnO) and La₂O₃ nanoparticles at concentrations above 1 wt.% provided highly water whitening-resistant coating films. Based on the results, the crosslink density was shown to have the greatest influence on the water whitening resistance of coatings.

Table 5: Comparison of optical properties of coating films before after water exposure

Sample	Before water exposure		Water whitening due to water exposure	
	Gloss (GU)	Transmittance (%) ^a	Transmittance (%) ^a	Decrease in transmittance (rel.%)
L ₀	79.9 ± 0.5	89.5	48.8	45.5
LMgO-0.5%	78.7 ± 0.8	90.1	53.9	40.2
LMgO-1%	78.4 ± 0.3	90.3	80.9	10.4
LMgO-1.5%	78.2 ± 0.5	89.7	85.3	4.9
LZnO-0.5%	80.0 ± 0.6	90.9	49.5	45.5
LZnO-1%	78.6 ± 0.4	90.0	58.3	35.2
LZnO-1.5%	78.6 ± 0.3	89.4	68.7	23.0
LMgO+ZnO-1.25%	79.7 ± 0.5	89.9	85.9	5.3
LMgO+ZnO-1.5%	79.9 ± 0.4	89.8	86.7	3.5
LMgO+ZnO-1.75%	79.9 ± 0.2	89.9	87.2	3.0
LLa2O3-0.5%	78.0 ± 0.2	90.1	54.5	39.5
LLa2O3-1%	77.3 ± 0.3	90.6	78.8	13.0
LLa2O3-1.5%	77.6 ± 0.2	89.6	87.6	2.2

^a Value was measured at 500 nm.

The results of physical-mechanical properties, chemical resistance, and resistance to flash corrosion of coating films are shown in Tab. 6. Measurements of the surface hardness showed that coating hardness is affected by the increasing concentration of incorporated MeO nanoparticles. Coatings with embedded ZnO nanoparticles exhibited a lower surface hardness at lower nanoparticle concentrations in comparison with the reference (blank) coating. This phenomenon can be attributed by two competing effects, which are hydroplasticization (reducing hardness) and ionic interfacial crosslinking (increasing hardness), both phenomena being induced by dissolved Zn(OH)₂ molecules. For the latexes containing MgO nanoparticles, a pronounced decrease in coating hardness was found. This was probably due to the significant hydroplasticization of the carboxy-functionalized emulsion copolymer induced by the high extent of dissolved Mg(OH)₂ in the aqueous dispersion medium, as discussed above. In contrast, in latex coating films containing La₂O₃ nanoparticles, a significant increase in surface hardness was found, which is probably due to a superior effect of ionic interfacial crosslinking (and increased rigidity of polymer chains) over hydroplasticization. The above-discussed competitive phenomena of hydroplasticization and ionic crosslinking can be very well observed in the case of latex coatings combining MgO and ZnO nanoparticles, where a reduced surface hardness was observed due to the presence of added MgO, which increased with increasing concentration of ZnO nanoparticles, i.e. the effect of hydroplasticization of latex particles was slightly suppressed by the growing influence of ionic crosslinking.

Testing of mechanical properties showed that all coating samples showed increased impact resistance in contrast to the reference L₀, which can be attributed mainly to hydroplasticization resulting in softening of the emulsion copolymer. Thus, latex coatings with MgO nanoparticles exceeded the maximum evaluation value compared to latex coatings containing only ZnO and La₂O₃ nanoparticles, which is consistent with surface hardness and MFFT results. Adhesion testing showed that all samples exhibited the maximum possible evaluation value and therefore it can be stated

that the type and concentration of the inserted nanoparticles did not reduce the adhesion of the coating film to the glass substrate.

The chemical resistance of the coating films was evaluated using the MEK test. Incorporation of nanoparticles was found to provide excellent MEK resistance of the coating films. This phenomenon was probably caused by the increased network density due to the formation of ionic bonds between the metal cations and the carboxyl groups of the polymer chains, as discussed above. Although latex films containing La₂O₃ nanoparticles showed a high crosslink density, their resistance to MEK was found to be lower than for coating films containing ZnO nanoparticles (having a slightly lower crosslink density compared to La₂O₃ latex coatings). This phenomenon can be explained by the trivalent nature of lanthanum in comparison with the divalent nature of magnesium and zinc ions, the former being able to bind more carboxyl groups. In this way, the La₂O₃-based network is mediated by fewer ionic crosslink junctions that are believed to be disrupted preferentially during the MEK test.

Table 6: Comparison of physical-mechanical properties, chemical resistance, and resistance to flash corrosion of coating films

Sample	Surface hardness (rel.%)	Mechanical properties		MEK resistance (strikes)	Flash corrosion ^c	
		Impact resistance (cm)	Adhesion (deg.)		ASTM D 610-85 (%)	Iodometric scale (deg.)
L ₀	29.7 ± 0.9	10	0 ^a	35 ± 7	>50 ^b	14
LMgO-0.5%	17.5 ± 1.0	> 100 ^a	0	223 ± 16	>50	10
LMgO-1%	16.0 ± 1.2	> 100	0	> 300 ^a	10	1
LMgO-1.5%	13.2 ± 0.8	> 100	0	> 300	3	1
LZnO-0.5%	24.6 ± 0.5	80	0	196 ± 14	>50	11
LZnO-1%	26.6 ± 0.7	45	0	> 300	16	1
LZnO-1.5%	31.3 ± 1.1	35	0	> 300	16	1
LMgO+ZnO-1.25%	15.3 ± 0.5	> 100	0	> 300	16	1
LMgO+ZnO-1.5%	17.4 ± 0.9	> 100	0	> 300	10	1
LMgO+ZnO-1.75%	19.8 ± 0.7	> 100	0	> 300	10	1
LLa2O3-0.5%	37.5 ± 0.8	20	0	58 ± 5	>50	10
LLa2O3-1%	40.0 ± 0.9	15	0	178 ± 19	30	9
LLa2O3-1.5%	41.5 ± 1.4	15	0	213 ± 20	30	8

^a Maximum evaluative value (representing the best property).

^b Minimum evaluative value (representing the worst property).

^c The results are given after performing an accelerated laboratory flash corrosion test.

The disadvantage of water-based lacquers and paints is also the formation of the so-called flash corrosion after their application to a metal substrate, especially steel. Flash corrosion was evaluated according to the Iodine scale, i.e. the coloration of the steel substrate by washing with Fe²⁺ ions, and according to the ASTM D 610-85 standard, which was used to monitor corrosion centers. Flash corrosion was monitored after applying a latex coating to a steel substrate, and further after subjecting the coating to an accelerated laboratory test (see Tab. 6). Before the accelerated test it was found that all types of nanoparticles provided increased resistance to flash corrosion with increasing concentration of embedded nanoparticles. Excellent results were provided in the systems containing MgO nanoparticles, where no corrosion centers or steel substrate staining were monitored at all concentrations of embedded MgO nanoparticles, also in the case of the combinations of MgO and ZnO nanoparticles. In contrast, the results of the accelerated laboratory test revealed that latexes containing ZnO and La₂O₃-based nanoparticles did not show any significant effect on the inhibition of flash

corrosion, while the latexes containing MgO-based nanoparticles provided a decrease in the number of microscopic corrosion centers with increasing MgO nanoparticle content. We are of the opinion that the pH value of the coating after the evaporation of ammonia (see pH data in Tab. 1) has an effect on the formation of flash corrosion. The effect of alkaline pH on flash corrosion was described in the literature [53] and can be predicted using Pourbaix diagrams.

The antimicrobial efficacy of all prepared coating films according to modified ISO 22196 showed that the antibacterial efficacy increased with increasing concentration of embedded inorganic nanoparticles (see Tab. 7). Furthermore, the tests revealed that for each MeO nanoparticle type at the highest concentration in a coating film (theoretically 1.5 wt. %, practically about 1.3 wt.%), the biocidal activity of coatings was achieved, except for the bacterium *E. faecalis*, against which only the coating containing the highest concentration of MgO nanoparticles showed biocidal activity. The undisputed resistance of *E. faecalis* to ZnO and La₂O₃ nanoparticles can be explained by its higher resistance to oxidative stress, as mentioned above. In contrast, the biocidal efficiency of latex films with MgO nanoparticles can be explained by the high alkalinity of the coating film (see pH data in Tab. 3), which creates an unfavourable environment for MOs and in addition, increases the activity of reactive oxygen species [49]. It should be emphasized here that the exact antimicrobial mechanism of nanoparticles has not yet been clearly elucidated, but lipid peroxidation, the formation of reactive oxygen species, the presence of metal cations destroying MO enzymes, or the internalization of nanoparticles have been assumed [54,55]. The alkalinity of latexes may also play a role.

Table 7: Results of antibacterial activity of coating films obtained using modified ISO 22196

Sample	Growth of bacterial colonies ^a							
	<i>S. aureus</i>	\emptyset	<i>E. coli</i>	\emptyset	<i>E. faecalis</i>	\emptyset	<i>K. pneumoniae</i>	\emptyset
L ₀	5, 5, 5	5	5, 5, 5	5	5, 5, 5	5	5, 5, 5	5
LMgO-0.5%	5, 3, 3	4	4, 5, 5	5	3, 4, 4	4	1, 4, 1	2
LMgO-1%	1, 1, 3	2	5, 5, 5	5	2, 3, 3	3	0, 0, 0	0
LMgO-1.5%	0, 0, 0	0	0, 0, 0	0	0, 0, 0	0	0, 0, 0	0
LZnO-0.5%	0, 2, 2	1	0, 0, 0	0	3, 3, 3	3	0, 0, 0	0
LZnO-1%	0, 0, 1	0	0, 0, 0	0	3, 3, 3	3	0, 0, 0	0
LZnO-1.5%	0, 0, 0	0	0, 0, 0	0	3, 3, 3	3	0, 0, 0	0
LMgO+ZnO-1.25%	4, 5, 4	4	5, 5, 5	5	4, 4, 4	4	5, 5, 4	5
LMgO+ZnO-1.5%	4, 3, 3	3	5, 5, 5	5	2, 3, 2	2	3, 3, 2	3
LMgO+ZnO-1.75%	0, 0, 0	0	1, 0, 0	0	1, 2, 1	1	0, 0, 0	0
LLa ₂ O ₃ -0.5%	4, 5, 4	4	3, 4, 4	4	4, 4, 4	4	5, 5, 5	5
LLa ₂ O ₃ -1%	1, 4, 4	3	0, 2, 2	1	4, 3, 3	3	5, 5, 3	4
LLa ₂ O ₃ -1.5%	0, 0, 0	0	0, 0, 0	0	1, 2, 2	2	0, 0, 0	0

^a The scale for assessing the growth of bacterial colonies: 0 – without the growth; 1 – the deductible amount on the 1st impression (individual colonies); 2 – the deductible amount on the 1st impression (connected colonies); 3 – the 2nd imprint of the recognizable colony, the 3rd imprint can be detected; 4 – the 3rd imprint of the recognizable colony; 5 – overgrown, continuous growth.

4.3. Anti-corrosion properties

From the evaluation of the corrosion resistance of the coatings, it can be concluded, that cross-linking due to the effect of inserted nanoparticles increases the corrosion resistance of coatings compared to systems without nanoparticles, but sufficient corrosion resistance was only achieved against humid atmospheres, where

latexes containing inorganic nanoparticles showed very good corrosion resistance compared to latexes without nanoparticles, as shown in Fig. 1, which is in good agreement with their higher crosslinking density, which plays a significant role towards the interdiffusion of water molecules into the coating.

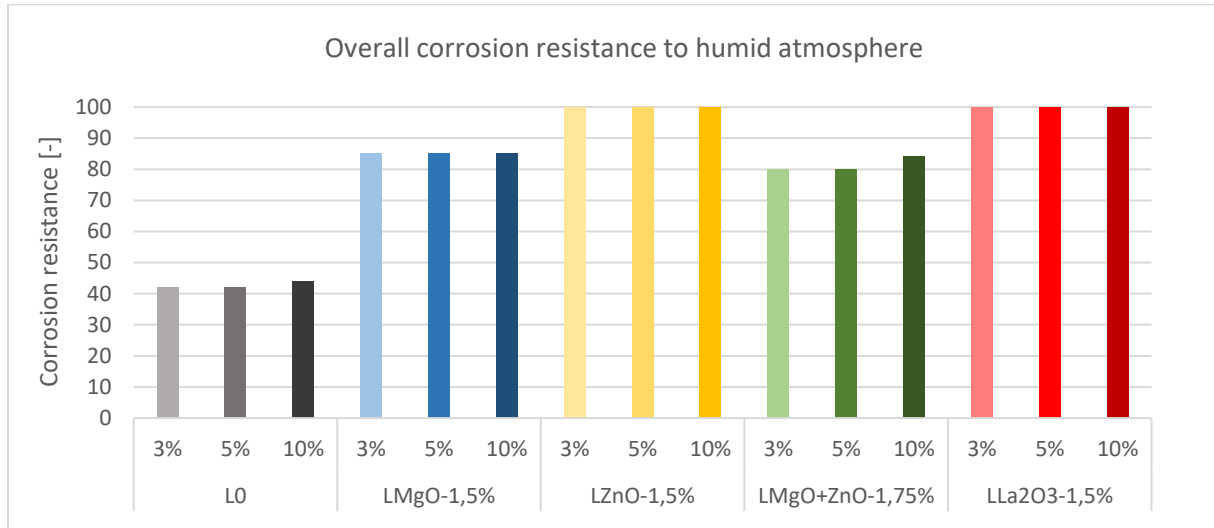


Figure 1 Overall corrosion resistance of anti-corrosion coatings to wet atmosphere after 480 hours of exposure

From the results obtained against neutral salt spray, it can be stated that cross-linking, due to the effect of embedded nanoparticles increases the corrosion resistance of coatings again, but it is insufficient to obtain anti-corrosion coatings with the required properties, and it is therefore necessary to choose pigments with high anti-corrosion efficiency to prepare anti-corrosion paints with corrosion resistance C3 and above, as can be seen from Fig. 2.

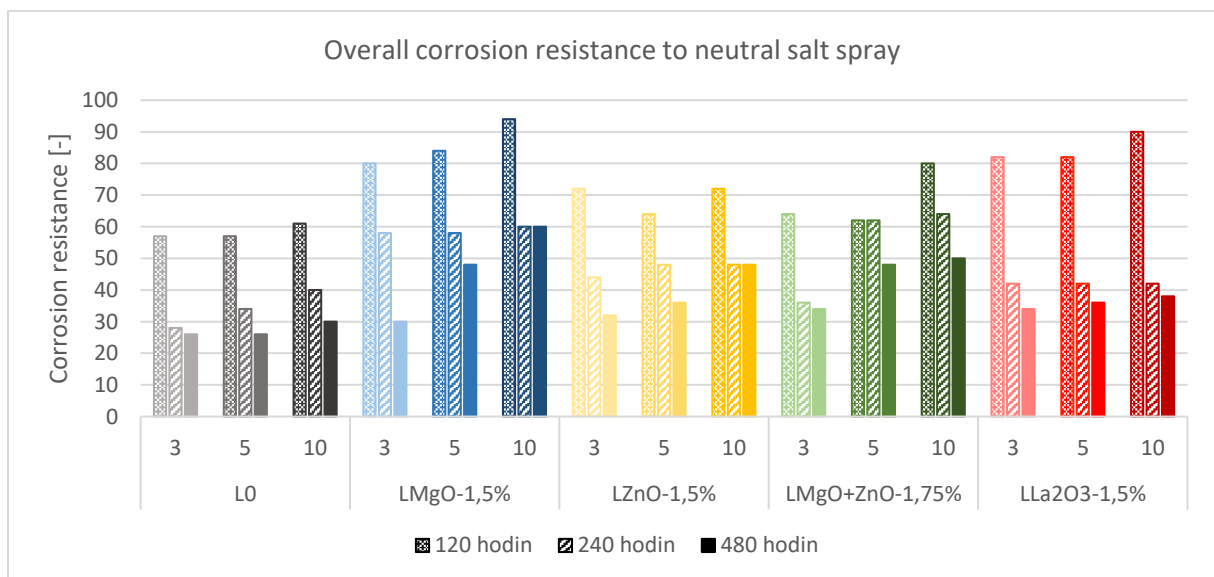


Figure 2 Overall corrosion resistance of anti-corrosion coatings to neutral salt spray after 480 hours of exposure

Conclusions

This work was devoted to the development of antimicrobial acrylate latexes which are expected to provide antimicrobial activity both in the liquid state and subsequently as a coating film on various substrates without the use of commercial (often toxic) biocidal additives. Various types of surface-untreated MeO nanoparticles have been used as functional antimicrobial additives, namely MgO, ZnO, La₂O₃, and combinations of MgO and ZnO. To overcome the typical shortcomings of acrylate latexes, keto-hydrazide interfacial crosslinking has been introduced into the latexes. The inorganic nanoparticles were inserted into the latex during semi-continuous emulsion polymerization and latexes prepared in this way showed long-term stability. It was found that all used MeO nanoparticles provided antimicrobial properties and at the highest concentration used (theoretically 1.5 wt.%, practically about 1.3 wt.% in a dry coating film, and about 0.5 wt.% in liquid latex) ensured InCan antimicrobial stability of liquid latexes and bactericidal activity of coatings against 3 of 4 tested bacteria (*S. aureus*, *E. coli*, and *K. pneumoniae*). Only the coatings with the highest concentration of inserted MgO nanoparticles (1.31 wt.%) provided bactericidal activity against *E. faecalis*, probably due to the high alkalinity of the coatings caused by the hydration of MgO. In contrast, only latex coatings containing ZnO nanoparticles showed fungicidal activity, which is probably related to the highest concentration of reactive oxygen species formed in the case of ZnO nanoparticles. In addition to antimicrobial activity, the incorporation of MeO nanoparticles into acrylate latex was shown to provide additional advantages. All types of inorganic nanoparticles were found to act as effective ionic crosslinkers, providing excellent resistance to MEK and water whitening without compromising the gloss and transparency of coatings. Furthermore, it was found that the incorporation of MgO nanoparticles into latex caused a significant decrease in MFFT due to hydroplasticization of the carboxy-functionalized emulsion copolymer, which was more pronounced with increasing concentration of MgO nanoparticles (converted predominantly to Mg(OH)₂). The insertion of MgO nanoparticles in latex also increased resistance to flash corrosion of steel substrates, including the number of microscopic corrosion centers, where at the highest concentration of nanoparticles, no corrosion center formation was evident, probably due to latex alkalinity. From the evaluation of the corrosion resistance of the coatings, it can also be concluded, that the cross-linking due to the effect of inserted nanoparticles increases the corrosion resistance of the coatings compared to systems without nanoparticles.

It can be concluded that environmentally friendly latex binders using MeO nanoparticles as antimicrobial additives and self-crosslinking agents were developed and these materials provide durable hygienic coatings suitable for the protection of various materials.

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