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Current Alternatives for In-can Preservation of Aqueous Paints: A Review †

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Abstract: With the transition towards more sustainable paint formulations based on waterborne environment, the susceptibility for microbial contamination has to be better controlled to increase shelf life and functional lifetime. However, recent restrictions in European regulation on use of biocides have put limitations on the concentrations for traditional systems providing either in-can or dry-film preservation. The commercial technologies for in-can preservation that are currently available are based on isothiazolines, such as 2-methyl-4-isothiazolin-3-one (MIT), 1,2-benzisothiazolin-3-one (BIT) and 5-chloro-2-methyl-4-isothiazolin-3-one (CMIT). At present, however, only limited number of alternatives can be used and are reviewed in this presentation. The examples of non-sensitizing biocidal components for coatings may include quaternary/cationic nitrogen amines, silver ion or zinc complexes. However, the use of the latter is not without risk for human health. Therefore, it is believed that disruptive methods will need to be implemented in parallel with more innovative bio-inspired solutions. In particular, the antimicrobial polymers, amino-acid based systems and peptides have similar functions in nature and can offer potential for antimicrobial activities. Also cross-border solutions currently applied in food or cosmetics industries should be considered as examples that need to be further adapted for paint formulations. However, the incorporation in paint formulations remains a challenge in view of the stabilization and rheology control of the system. This work's overview aims to provide different strategies and best evidence for future trends.

Keywords: paint; anti-microbial; biocide; preservation

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1. Introduction

Waterborne paint formulations have been introduced in a response towards more eco-friendly solutions reducing the application of chemical solvents and lowering VOC emissions. In parallel, however, the aqueous environment is beneficial for growth and survival of micro-organisms such as bacteria, fungi and yeast. Their origin can be related to the selection of raw materials and different contamination sources in the processing plant. In a particular study, microbial contamination of the paint with *Pseudomonas* as the predominant genus mainly occurred as a result of biofilm formation in the production equipment [1]. In another study, sufficient screening and appropriate selection of the raw materials was advised in order to reduce contamination [2]. The degradation of paints in presence of micro-organisms is noticed as a change in color, penetrating odor, gas formation, reduced stability, pH variations and viscosity reduction. The quality loss of the paint finally results in product spoilage and time delay. Although the presence of bacteria can be controlled through better material selection and plant hygiene, they cannot be fully avoided. Therefore, in-can preservation (PT-6) is required to ensure a long in-pot lifetime, which is industrially expected to be at least 3 years.

The use of biocides for in-can preservation (PT-6), which are inherently toxic and potentially affecting human health, has been subjected to more stringent legislation in

recent years, following the Biocidal Products Regulation (updated March 2020). In the early years, organo-mercury compounds and formaldehyde biocides have been banned because of carcinogenic effects. Following risk assessment studies, the diverse range and different potential of formaldehyde-condensate compounds in regard to formaldehyde gas were recognized and taken into account for preservatives. While some standards for paints and coatings (Green Seal GS-11) prohibit the release of free formaldehyde, others have restricted the emission of free formaldehyde at below 100 ppm. The isothiazolinone derivatives were introduced as formaldehyde-free alternatives for both in-can and dry-film preservation, including 1,2-benzisothiazolin-3-one (BIT), 2-methylisothiazol-3(2H)-one (MIT), 2-octyl-2H-isothiazol-3-one (OIT), 5-chloro-2-methyl-4-isothiazolin-3-one (CMIT) and 4,5-dichloro-2-n-octyl-3(2H)-isothiazolone (DCOIT) (Figure 1) [3]. Nevertheless, the observations of allergic skin reaction towards one specific type of isothiazoline, i.e. MIT, lead to the classification as skin sensitizer and reduction in specific concentration limits below 15 ppm according to the Risk Assessment Committee (RAC) of the European Chemicals Agency (ECHA). In view of a harmonized classification, concerns rise on the use of other isothiazolines at low dosages (< 15 ppm) that are inefficient for their activity as in-can preservative. In parallel, the present options for alternative preservatives are limited through the Article 95 List in which 52 active ingredients are listed and only 15 are compatible with paints and coatings [4]. Therefore, the availability of biocides for in-can preservation becomes restricted and poses high pressure on industrial applications.

Present solutions on short-term are limited and long-term developments should take into account novel preservation systems, as reviewed in this contribution. This overview focusses on compositional aspects of waterborne paints or latex (e.g. acrylates) and does not detail additional measurements that can be taken to enhance paint preservation, such as raw material screening, pasteurization, thermal treatments, plant hygiene and anti-septic packaging. Also alternative systems such as high-pH paints or dispersible powder paints are not further discussed.

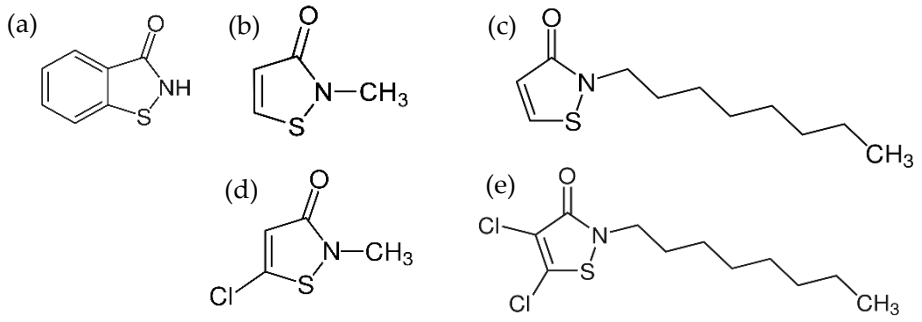

Figure 1. Isothiazolinones presently used in industry for in-can preservation of paint, (a) BIT (CAS 2634-33-5), (b) MIT (CAS 2682-20-4), (c) OIT (CAS 26530-20-1), (d) CMIT (CAS 26172-55-4), (e) DCOIT (CAS 64359-81-5).

2. Current industrial trends in preservation of waterborne paint

2.1 Blending of biocide formulations

The framework for reducing concentrations of isothiazolines is set by the required inhibitory concentrations of MIT and BIT in order to function as an efficient biocide (Table 1) [5]. For most single biocides, the minimum inhibitory concentration (MIC) is above the threshold value for selected laboratory strains, whereas even a higher concentration might be necessary in practice to mitigate wild strains [6]. Otherwise, it should be noticed that some biocides have deficiencies or 'gaps' in their performance, such as e.g. the limited anti-fungal properties of BIT and MIT. By using biocide blends, a synergistic effect in biocidal

properties was observed with impressive decrease in minimum inhibitory concentrations, below regulatory limits. In parallel, the chance for developing resistance and tolerance of bacteria against biocides significantly reduces when exposed to blends rather than single active ingredients [7]. Bacteria originating from biofilms are indeed known to have significantly increased tolerance towards common biocides used for in-can preservation and the minimum inhibitory concentrations are indeed exceeded in paints. The biocide blending also allows to combine biocides with both short-term activity (e.g. O-formals, CMIT) and long-term protection (e.g., BIT). By selecting a combination of active ingredients within an optimum concentration ratio, compatibility can be created including pH, redox potential. The two most promising and versatile platforms for in-can preservation are based on a combination of MIT/BIT in ratio 1:1 (for pH ranges between 2 and 11), or CMIT/MIT in ratio 3:1 (for pH ranges below 8) [8]. By utilizing MIT/BIT and CMIT/MIT blends, new generations of in-can biocides were industrially developed that can outperform traditional biocides by a factor of two or more without cautionary labelling related to the European legislation [9]. In such formulations, the CMIT and MIT can be used in concentrations below 15 ppm [10]. However, the CMIT has also been identified as a skin sensitizer at concentrations above 64 ppm.

Table 1. Biocide activity (MIC values) of isothiazolines and their blends against laboratory-scale organism cultures [5, 6]**.**

Organism	**Minimum inhibitory concentration (MIC) (ppm)**				
	BIT	**MIT**	**CMIT**	**MIT/BIT**	**CMIT/MIT**
Escherichia coli (b)	25	17.5		10	9.0
Klebsiella pneumoniae (b)	25	20		15	9.0
Pseudomonas aeruginosa (b)	150	30	0.6	20	11.2
Pseudomonas putida (b)	60	12.5	0.2	10	
Pseudomonas stutzeri (b)	20	12.5		10	
Aspergillus niger (m)	100	750		50	9.0
Candida albicans (y)	200	75			9.0

b = bacteria, m = moulds, y = yeast

The blending of isothiazolines with 2-bromo-2-nitro-1,3-propanediol (bronopol), in particular with CMIT/MIT, was used to improve the efficiency of MIT at low concentrations. Dosages for those systems can vary with sample preparations, e.g., from 60 ppm bronopol + 10 ppm CMIT/MIT to 200 ppm bronopol + 33 ppm CMIT/MIT depending on the severity of the contamination and the substrate. A concentration ratio of 6:1 bronopol to CMIT/MIT was recommended [11], whereas the dosage levels of CMIT/MIT could be reduced from typically 20 to 30 ppm towards 7.5 to 15 ppm. The bronopol has been utilized in situations to control bacteria that have developed tolerance or resistance against other biocides based on fomaldehyde or isothiazolines. Recently, the interest in bronopol was mainly raised for headspace preservation.

The combinations of BIT with pyrithione (PT) active agents, which are known as traditional fungicides, are finding increased use as co-biocides for in-can preservation of latexes. The pyrithiones interact with the microbial membranes as a chelating agent and disrupting essential ion gradients. However, only specific Zn-pyrithiones (ZPT) or Na-pyrithiones (NPT) are applicable as other cations result in strong coloration. The chelation complexes with Fe^{2+} or Cu^{+} ions result in insoluble compounds and blue color for only small concentrations of ions present. The pass levels in antimicrobial testing for sample formulations of 2% BIT + 8 % NPT, 2% BIT + 4 % NPT were efficient at biocide concentrations of 0.10 %, while they could be used up to a maximum concentration of 0.25 % with acceptable BIT level [12]. In particular, the BIT/ZPT blend is an efficient biocide against *Pseudomonas* bacteria that are more resistant against other preservatives (see Table 1).

The other types of biocide were added as co-preservatives to enhance the performance of CMIT/MIT and BIT at low dosages, such as 2,2-dibromo-3-nitrilopropionamide (DBNPA), dichloro-2-n-octyl-4-isothiazoline-3-one (DCOIT), sorbate, sodium benzoate, o-phenylphenol sodium salt or carbamate [13]. However, some of them are problematic due to various reasons related to the specific biocide/fungicide activity, color, hydrolysis, or requirement of high concentrations. Although covering a broad activity range against Gram-positive and Gram-negative bacteria, yeast, fungi and algae, the DBNPA is only known for fast and short-time activity. Otherwise, new micro-emulsion technologies need to be developed for using DCOIT.

2.2 Metal-based additives

The antimicrobial properties of metal-oxide nanoparticles have been demonstrated in several fields such as textiles, packaging, cosmetics or biomedical applications. Paint formulators have mainly introduced silver ions or silver nanoparticles. The silver ions directly interact with the bacterial metabolism, thereby preventing the conversion of nutrients into energy and inhibiting the survival, reproduction and colonization of bacteria. The silver additives can be based on silver phosphate glass active ingredients, and silver ions are most effective against a broad spectrum of bacteria. However, the in-can preservation with silver ions requires high ion concentrations to be efficient and in relation with their high cost, the industrial application of this technique remains limited. Therefore, it is more attractive in use for dry-film protection, where it also presents anti-fungal properties when used as additive in waterborne acrylic indoor paints [14].

Other metal oxides such as ZnO, TiO_2, SiO_2 or MgO have additional photocatalytic activity and can release reactive oxygen substances to kill bacteria under UV radiation. In particular, the zinc oxide and/or other zinc complexes were used as dry-film preservative in exterior coatings to reduce fungi and algae growth. The addition of ZnO nanoparticles in a waterborne acrylic latex coating provided stable dispersions with enhanced physico-chemical, mechanical and anti-corrosive properties in parallel with antimicrobial resistance at lower biocide content compared to commercial paints [15]. Indeed the acrylic paints may benefit from ZnO nanoparticles with antimicrobial properties and low toxicity [16], while the active role of the oxide species may be further enhanced through the combination of ZnO nanoparticles in oxide/amine composites added into the acrylic paint [17]. Alternatively, the interior paints of water-based acrylate dispersions with MgO nanoparticles provide antimicrobial properties due to the morphology of the nanoparticles having sharp edges and formation of reactive oxygen species that induce the peroxidation of lipids in the bacterial cell [18]. The functionalized SiO_2 mostly showed an effect against algal growth in dry paints and was more beneficial due to its non-leaching properties [19]. However, the future application of nanotechnology based on metal nanoparticles should be evaluated against toxicity risk assessment.

Therefore, it is an option to shift towards naturally-based nanoparticles with demonstrated antibacterial properties in waterborne polyurethane systems, including clay-based minerals. The halloysite nanotubes were formulated with encapsulated carvacrol and allowed for the sustained release and antibacterial activity over longer term [20].

3. Novel bio-based trends in preservation of waterborne paint

The need to reflect on alternative preservation mechanisms away from traditional isothiazolines is given by the facts that:

(i) all types of isothiazolines are inherent skin sensitizers, although at different concentration levels. The classification of MIT as skin sensitizer and reduction in exposure concentrations might set a precendent for other types such as CMIT, CMIT/MIT and BIT finally leading to a homogenized legislation and reduction in

use of all isothiazolines. In parallel, the eventual scarcity in supply and ban of common isothiazolines implies a threat on paint industry.

(ii) micro-organisms develop increased tolerance against isothiazolines and need exposure to different classes of biocides.

Apart from current industrial approaches, more sustainable innovations for in-can preservation are to be expected by the implementation of bio-based compounds. The development of novel mechanisms can be inspired through natural antimicrobial systems. Some natural polymeric materials exhibit antimicrobial activity, which can be considered for in-can preservation of paints. The presented solutions, however, are not yet common practice in paint industry but are promising for disruptive changes in preservation technology. Indeed, the development of novel in-can preservation would need appropriate development time and resources. The inspiration for natural preservatives can be found in the application in cross-domains such as cosmetics or food preservation, where commonly applied natural preservatives include plant extracts, chitosan or oligosaccharide derivatives, bacteriocins, bioactive peptides and essential oils.

3.1 Acids

The use of mild bio-based and/or biodegradable organic acids and combinations thereof are applied in cleaning, disinfection, food and personal care products. Their antibacterial mechanisms are based on a combination of effects, either interacting with the bacterial cell membrane, or acting as a chelating agent for sequestration of nutrients. The acid conditions disrupt the cell regulation at a general level and inhibit the fermentation processes thus preventing bacterial growth. The amphiphilic nature and combination with other acids or surfactants often enable interactions with the cell membrane (lipid bilayer) and enhance the cell permeability. For use as in-can preservative, the acids are compatible with low pH of paint formulations and performances can be further boosted in combination with formulation additives.

The lactic acid is a plant-based active ingredient against gram-negative bacteria and is compatible with paint formulations including a cationic surfactant system at pH below 4.5 [21]. The preservative effect of lactic acid can be attributed to the production of antimicrobial substances such as hydrogen peroxide and creation of an acidic environment through organic acids. The concentration affinity of lactic acid against fifty strains was demonstrated, retaining its inhibitory effect at low pH induced by the acid environment up to neutral pH [22]. The zinc lactate is a zinc salt derived from the lactic acid that also combines antimicrobial properties against bacteria and yeasts [23].

The use of other acids such as caprylhydroxamic acid, benzoic acid, sorbic acid and its combination with polyols such as glyverin, propylene glycol, propanediol or hexane diol rely on the creation of multiple barriers against microbial growth and tunability against a broad spectrum of antimicrobial control [24].

3.2 Anti-microbial polymers

The cationic polymers bearing positive charges and their assemblies may generally serve as favourable anti-microbial compounds [25]. The presence of quaternary ammonium groups in a polymer structure is a well-known example, as it also occurs in nature. Alternatives include polymer compounds with halogens, phosphor, sulphonates, organometalic polymers and phenol or benzoic acid [26]. The cationic amines are likely available as industrial materials, however, the incorporation of cationic biocides into an acrylic paint formulation is challenging and requires additional chemical modification, as most of the water-based paints are anionically stabilized. As such, an antimicrobial waterborne polyurethane paint was developed by transformation into a quaternary ammonium salt emulsion [27]. The modified paint also shows better dispersion stability

and small particle sizes in parallel with hydrophobic properties enhancing antimicrobial effects, which can be regulated by selection of a chain extender with long hydrocarbon tail. In particular, the quaternizing of tertiary amines with different alkyl bromides was systematically investigated and indicated higher killing efficiency for bacterial and fungal strains with increasing length of the alkyl chain [28]. The waterborne poly(methacrylate) suspensions were prepared with this type of antimicrobial hyper-branched emulsifier. Other cationic acrylate emulsions with antimicrobial copolymers were synthesized using alternative quaternary ammonium compounds or ammounium chloride derivates [29].

Chitin is a natural biopolymer recovered through extraction from crustacean with intrinsic anti-microbial properties. The chitosan has reactive amino groups on its pyranose ring and becomes a cationic polymer upon protonation of the amino groups. However, chitosan simply added to waterborne coatings cannot uniformly disperse. Furthermore, when chitosan-acid solution is added to waterborne coatings using acrylic emulsions, precipitates are formed because chitosan is a cationic polymer. Therefore, the incorporation of chitosan in paint formulations has been rarely considered yet, but one method for preparation of a hybridized chitin-acrylic emulsion was developed through emulsion polymerization and optimization of the pre-emulsification methods. When the products were applied as interior finishing, a reduction in formaldehyde content of the paint was observed [30]. The synthesis by emulsion polymerization of an acrylic resin with a quaternary ammonium salt (hybrid chitosan/acrylic resin emulsion) also resulted in better stability and less leaching due to better cross-linking between the acrylic resin particles [31]. The polyurethane paints could also be modified with addition of chitosan/bentonite nanocomposites to improve anti-microbial properties [32]. As a more advanced approach, emulsion paints were modified through the addition of chitosan-grafted acrylic acid [33]. The chitosan-grafted acrylic acid was then used as an additive in a modified emulsion paint, with a general performance presenting higher density, more flexibility, better adhesion to the substrate and shorter drying times. In particular, the antimicrobial performance of the wet paint benefits from the presence of chitosan, depending on the obtained grafting efficiency and concentrations of the grafted acrylic acid.

3.3 Bio-engineered enzymes and peptide-based polymers

The enzymes that can be used as additives will assist in the inhibition of bacterial growth, e.g. through degradation of the cell wall (lysozymes), interaction with the biofilm or glycocalyx (alginate lyase), or generation of reactive oxygen species (glucose oxidase). The glucose oxidase favours the oxidation of glucose and release of hydrogen peroxide that creates damage of the cell wall and destruction of lipids, proteins and sugars. The synergistic effects of bio-based biocides such as glucose oxidase or lysozymes added to traditional paints with MIT biocide were demonstrated [34], allowing to facilitate the activity and reduce the required concentrations of MIT.

The antimicrobial peptides (AMP) typically have a length of 6 to 7 amino acids and have inherent activity against bacteria, fungi and molds depending on the selection of peptide sequences from library. The cationic peptides are particularly designed with net positive charge (e.g., arginine, lysine, histidine) in combination with hydrophobic amino acids (e.g., leucine, phenylalanine). The biocidal activity of AMP can be related to permeation and disruption of the nuclear membrane. The screening of hexapeptides (AMP-6) and heptapeptides (AMP-7) as in-can preservatives for styrene-acrylic latex showed synergistic effects with concentrations of MIT below 15 ppm [35]: the AMP-6 showed best activity against fungi, while AMP-7 was satisfactory against both bacteria and fungi. A reduction in cellular metabolism of about 50 % was observed when added in a range of concentrations from 0.5 to 0.005 mg/ml. In future, it is believed that the available database with diversity of peptides and access to large-scale synthetic production will allow to adapt the antimicrobial activity of AMP for different paint systems.

3.4 Antimicrobial nanocellulose

The addition of nanocellulose in waterborne coatings has been recently studied and confirmed better service life of the wood surfaces in parallel with higher mechanical resistance [36]. As a waterborne agent, it enables the control of paint rheology in addition to improvements in antifouling and antibacterial properties after surface modification [37]. The antimicrobial properties of nanocellulose against bacteria, fungi and algae can be tuned with functional groups such as aldehydes, quaternary ammonium, metal oxide nanoparticles as well as chitosan [38]. Although mostly suggested to be used as antimicrobial paint, the nanocellulose is also compatible with waterborne acrylic dispersions where the cellulose nanofibers (CNF) could be homogeneously mixed after facile mixing with small concentrations of aminopropyl-triethoxysilane under ultrasonic treatment and stirring [39]. The cationic or zwitterionic properties of modified nanocellulose after surface modification with chemical grafting or adsorption of polyelectrolyte layers by electrostatic self-assembly may introduce the antimicrobial properties. In contrast, the mixing of cellulose nanocrystals (CNC) could be prepared more straightforward as a reinforcement filler in waterborne coatings. Besides a better mechanical reinforcement and barrier properties with a dense fibrillar network of CNF, however, the acrylate/CNF dispersions present significant increase in viscosity [40]. As such, the nanocellulose serves as multifunctional bio-based ingredients for waterborne paint formulations.

4. Conclusion

In view of more strict regulation on biocides, the preservation of waterborne paint formulations is a huge challenge for coatings and paint industries. Present solutions at industrial scale focus on the decrease in minimum inhibitory concentrations for isothiazolines through blending. The opportunities for disruptive and innovative technologies are offered from bio-inspired materials, but will certainly need longer development time.

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References

1. Lorenzen, J.; Poulsen, S. Eco-friendly production of waterborne paint. The Danish Environmental Protection Agency, Odense (Denmark), **2021**.
2. Kharadi, N.; Mistry, R. Economic impact of losing effective in-can preservatives. International Association for Soaps, Detergents and Maintenance Products, London (UK), **2018**.
3. Silva, V.; Silva, C.; Soares, P. ; Garrido, E.M. ; Borges, F. ; Garrido, J. Isothiazolinone biocides: chemistry, biological and toxicity profiles. *Molecules* **2020**, *5*, 991.
4. Müller, A.; Schmal, V.; Gschrei, S. Survey on alternatives for in-can preservation for varnishes, paints and adhesives. Federal institute for occupational safety and health, Berlin (Germany), **2020.**
5. Paulus, W. Relationship between chemical structure and activity or mode of action of microbiocides. In *Directory of microbiocides for the protection of materials*; Paulus, W. Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2004; pp. 9-22
6. Gillatt, J.; Julian, K.; Brett, K.; Goldbach, M.; Grohmann, J.; Heer, B.; Nichols, K.; Roden, K.; Rook, T.; Schubert, T.; Stephan, I. The microbial resistance of polymer dispersions and the efficacy of polymer dispersion biocides – A statistically validated method. *Int Biodeter Biodegrad* **2015**, *104*, 32-37.
7. Wales, A.D.; Davies, R.H. Co-selection of resistance to antibiotics, biocides and heavy metals, and its relevance to foodborne pathogens. *Antibiotics* **2015**, 4, 567-604.
8. Kim, M.J., Lim; K.B., Lee, J.Y., Kwack, S.J., Kwon, Y.C., Kang, J.S., Kim, H.S., Lee, B.M. Risk assessment of 5-chloro-2-methylisothiazol-3(2h)-one/2-methylisothiazol-3(2h)-one (cmit/mit) used as a preservative in cosmetics. *Toxicol Res* **2019**, *35*, 103-117.

9. Betancur, J.; Browne, B.A. Innovating in-can preservatives depends on finding and testing the perfect blend. *Paint Coat Ind* **2021**, *17*, 8-15.
10. Rees, R. Guidance on the use of globally-relevant modern biocides. In: Technical Papers by the pressure sensitive tape council, Vol. 38, 2013, pp 1-5.
11. BASF, Industrial product preservation, Ludwigshafen (Germany), 2000.
12. Brown, S.A. Past, present, and future options for preservative in coatings. *Coatings World* **2017**, *3*, 1-5.
13. Chervenak, M.C.; Konst, G.B.; Schwingel, W. Non-traditional use of the biocide DBNPA in coatings manufacture. *JCT Coat Tech* **2005**, *2*, 38-42.
14. Bellotti, N.; Romagnoli, R.; Quintero, C.; Dominguez-Wong, C.; Ruiz, F.; Deya, C. Nanoparticles as antifungal additives for indoor water borne paints. *Prog Org Coat* **2015**, *86*, 33-40.
15. Dankova, M.; Kalendova, A.; Machotova, J. Waterborne coatings based on acrylic latex containing nanostructured ZnO as an active additive. *J Coat Technol Res* **2020**, *17*, 517-529.
16. Fiori, J.J.; Silva, L.L.; Picolli, K.C.; Ternus, R.; Ilha, J.; Decalton, F.; Mello, J.M.M.; Riella, H.G.; Fiori, M.A. Zinc oxide nanoparticles as antimicrobial additive for acrylic paint. *Mater Sci Forum* **2017**, *899*, 148-253.
17. Kamal, H.B.; Antoniuos, M.S.; Mekewi, M.A.; Badawi, A.M.; Gabr, A.M.; El Bagdady, K. Nano ZnO/amine composites antimicrobial additives to acrylic paints. *Egypt J Petrol* **2015**, *24*, 397-404.
18. Steinerova, D.; Kalendova, A.; Machotova, J.; Pejchalova, M. Environmentally friendly water-based self-crosslinking acrylate dispersion containing magnesium nanoparticles and their films exhibiting antimicrobial properties. *Coatings* **2020**, *10*, 340.
19. Dileep, P.; Jacob, S.; Narayanankutty, S.K. Functionalized nanosilica as an antimicrobial additive for waterborne paints. *Prog Org Coat* **2020**, 142, 105574.
20. Hendessi, S.; Sevinins, E.B. ; Unal, S. ; Cebeci, F.C. Menceloglu, Y.Z. ; Unal H. Antibacterial sustained-release coatings from halloysitenanotubes/waterborne polyurethanes. *Prog Org Coat* **2015**, *101*, 263-261.
21. Stanojevick-Nikolic, S.; Dimic, G.; Mojovic, L.; Pejin, J.; Djukic-Vukovic, A.; Kocic-Tanackov, S. Antimicrobial activity of lactic acid against pathogen and spoilage microorganisms. *J. Food Proc Pres* **2015**, *40*, 990-998.
22. Pasricha, A.; Bhalla, P.; Sharma, K.B. Evaluation of lactic acid as an antibacterial agent. Indian J Dermatol Venereol Leprol **1979**, *45*, 159-161.
23. Amrouche, T.; Noll, K.S.; Wang, Y.; Huang, Q.; Chikindas, M.L. Antibacterial activity of subtilosin alone and combined with curcumin, poly-lysine and zinc lactate against listeria monocytogenes strains. *Probiotic Antimicr Prot* **2010**, *2*, 250-257.
24. Garcia, M.; Sol, C.; de Nova, P.; Puyalto, M.; Mesas, L. et al. Antimicrobial activity of a selection of organic acids, their salts and essential oils against swine enteropathogenic bacteria. *Porc Heatlh Managm* **2019**, *5*, 32.
25. Ribeiro, A.M.; Carrasco, L.D. Cationic antimicrobial polymers and their assemblies. *Int J Mol Sci* **2013**, *14*, 9905-9946.
26. Kamaruzzaman, N.F.; Tan, L.P.; Hamdan, R.H.; Choong, S.S.; Woing, W.K.; Gibson, A.J.; Chivu, A.; Pina, M. Antimicrobial polymers: the potential replacement of existing antibiotics. *Int J Mol Sci* **2019**, *20*, 2747.
27. Wang, Y.; Chen R.; Li, T.; Ma, P.; Zhang, H.; Du, M.; Chen, M.; Dong, W. Antimicrobial waterborne polyurethanes based on quaternary ammonium compounds. *Ind Eng Chem Res* **2020**, *59*, 458-463.
28. Zhao, P.; Mecozzi, F.; Wessel, S.; Fieten, B.; Driesse, M.; Woudstra, W.; Busscher, H.J.; Mei, H.C.; Loontjens, T.J.A. Preparation and evaluation of antimicrobial hyperbranched emulsifiers for waterborne coatings. *Langmuir* **2019**, *35*, 5779-5786.
29. Wu, Y.; Gan, J.; Yang, F.; Zhang, H.; Wang, W. Preparation and antibacterial properties of waterborne UV cured coating modified by quaternary ammonium compounds. *J Appl Polym Sci* **2021**, *138*, 50426.
30. Wada, T.; Uragami, T.; Matoba, Y. Chitosan-hybridized acrylic resins prepared in emulsion polymerizations and their application as interior finishing coatings. *JCT Res* **2005**, *2*, 577-592.
31. Wada, T.; Yasuda, M.; Yako, H.; Matoba, Y.; Uragami, T. Preparation and characterization of hybrid quaternized chitosan/acrylic resin emulsions and their films. *Macromol Mater Eng* **2007**, *292*, 147-154.
32. Rihayat, T.; Satriananda, S. Nurhanifa, R. Influence of coating polyurethane with mixture of bentonite and chitosan nanocomposites. *AIP Conf Proc* **2018**, *2049*, 020020.
33. Abolude, O.I. Modification of emulsion paint using chitosan-grafted acrylic acid. M.Sc. Thesis, Ahmadu Bello University, Zaria, Nigeria, 2016.
34. Hodges, T.W., Kemp, L.K.; McInnes, B.M.; Wilhelm, K.L.; Hurt, J.D.; McDaniel, S.; Rawlins, J.W. Proteins and Peptides as Replacements for Traditional Organic Preservatives. Coatings Tech **2018**, *15*, 45-50.
35. McDaniel, S.; McInnis, B.M.; Hurt, J.D.; Kemp, L.K. Biotechnology meets coatings preservation. *Coatings World* **2019**, *12*, 33-42.
36. Kluge, M.; Veigel, S.; Pinkl, S.; Henniges, U.; Zollfrank, C.; Rössler, A.; Gindl-Altmutter, W. Nanocellulosic fillers for waterborne wood coatings: reinforcement effect on free-standing coating films. *Wood Sci Technol* **2017**, *51*, 601-613.
37. Aguilar-Sanchez, A.; Jalvo, B. ; Mautner, A.; Nameer, S.; Pöhler, T.; Tammelin, T.; Mathew, A.J. aterborne nanocellulose coatings for improving the antifouling and antibacterial proper-ties of polyethersulfone membranes. *J Membrane Sci* **2021**, *620*, 118842.
38. Norrahim, M.; Nurazzi, N.M.; Jenol, M.A.; Farid, M.A.; Janudin, N.; Ujang, F.A.; Yasim-Anuar, T.A.; Najmuddine, S.U.; Ilyasf, R.A. Emerging development of nanocellulose as an antimicrobial material: an overview. *Mater. Adv.* **2021**, *2*, 3538-3551.
39. Tan, Y.; Liu, Y.; Chen, W. ; Liu, Y. ; Wang, Q.; Li, J.; Yu, H. Homogeneous dispersion of cellulose nanofibers in waterborne acrylic coatings with improved properties and unreduced transparency. *ACS Sus Chem Eng* **2016**, *4*, 3766-3772.
40. Hassan, M.L.; Fadel, S.M.; Hassan, E.A. Acrylate/nanofibrillated cellulose nanocomposites and their use for paper coating. *J Nanomater* **2018**, 4963834.