Eur. J. Wood Prod. (2014) 72:285–288
DOI 10.1007/s00107-013-0776-2

BRIEF ORIGINALS KURZORIGINALIA

Antimicrobial efficacy of silver nanoparticles in transparent wood coatings

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Received: 4 November 2013 / Published online: 12 January 2014

Abstract Results on the antimicrobial efficacy of silver nanoparticles in transparent wood coatings for outdoor application are presented. The performance of different hydrophobic, transparent coating systems with and without silver was studied during 2 years of natural weathering. In addition, laboratory efficacy tests were carried out on non-weathered and weathered specimens to assess the resistance of the coatings against mold, blue stain and algae. The protective effect of the tested silver containing coatings against common microorganisms was insufficient, even under initial, non-weathered conditions. Reasons for the failure are the inadequate initial silver concentrations below 50 ppm in the coatings and the associated insufficient availability of free silver ions on the coating surface.

Antimikrobielle Wirkung von Nanosilberpartikeln in transparenten Holzbeschichtungen

1 Introduction

The trend to increase the energy efficiency of buildings by using thick thermal insulation layers results in colder external surfaces and consequently enhances moisture condensation on the outer building envelope. Therefore, the demand for functional coatings to avoid growth of microorganisms is increasing. On the other hand, there is a general environmental discussion about organic biocides and the intention to reduce their use in coating products. Based on its strong toxicity among a wide range of microorganisms combined with low toxicity to humans, silver appears to be a possible alternative. While many reports on the effectiveness of silver against bacteria are available (Fabrega et al. 2011; Marambio-Jones and Hoek 2010; Musee et al. 2011), information about the protective effect of silver in wood façade coatings especially against mold and blue stain are rare (Plaschkies et al. 2010). Data about experiences during natural weathering are completely missing.

To extend the knowledge in this respect, the functionality and the safety of silver nanoparticle (Ag-NP) containing, hydrophobic and transparent coating systems for outdoor applications on wooden façade elements was investigated, and the results were compared with biocide free and organic biocide containing coatings. The results regarding functionality are presented and discussed in this Brief Original.

More detailed information about the project is given in Künniger et al. (2011). Additional comprehensive information on the environmental impact, especially the loss of active substances (silver and organic biocides) during weathering into the runoff water and their toxicity to different water organisms are published in Künniger et al. (2014).

2 Materials and methods

Laboratory scale façade elements (horizontal planking) with an area of $0.75 \times 1.44\ m^2$ and $0.63 \times 0.35\ m^2$, respectively, were produced from industrially manufactured lamellas made of Norway spruce (*Picea abies*). Five different water-based, transparent and hydrophobic coating

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Table 1 Coating systems and properties
Tab. 1 Beschichtungssysteme und deren Eigenschaften

	HySiwAg	HySi	OARwAg	AARwB	ARwB
Type	Hydrolysed Silane	Hydrolysed Silane	Oily Alkyd Resin	Alkyd/Acryl Resin	Alkyd Resin
Biocide	Ag-NP (Ø 10–30 nm) 46 ppm	None	Silver 2 ppm	Propiconazole 2.28 w % IPBC 0.18 w %	IPBC, DCOIT and OIT all <1.25 w %
Film forming	No	No	Yes ~40 µm	Yes ~50 µm	Yes ~100 µm
Contact angle with water	~138°	~141°	~94°	~103°	~98°

systems (Table 1) were selected and applied according to the manufacturer recommendations. All five products were commercially available and, except for HySi, labeled as antimicrobial. As a benchmark, additional reference elements without surface treatments were produced. The end-grain surfaces of the lamellas were sealed with a 2P-PU paint to avoid fungal growth starting from the end-grain.

2.1 Natural and artificial weathering

The façade elements were installed vertically on metal racks at Empa premises and exposed to SW (220°) direction from June 2009 to June 2011.

The large façade elements were observed regarding the overall performance of the coatings, especially their resistance to growth of microorganisms. All façade elements were visually examined at regular intervals during the time of natural weathering.

The smaller façade elements were removed after 2 months for subsequent laboratory efficacy tests.

Artificial weathering included four cycles. Each cycle consisted of 3 h radiation and 40 °C surface temperature, followed by 0.5 h sprinkling with around 40 l water and finally 2.5 h conditioning at 20 °C and air dehumidifying. The radiation in the weathering chamber was performed using 20 daylight bulbs 'Ultra Vitalux' (bulb specification: 13.6 W/h UVA 315–400 nm and 3.0 W/h UVB 280–315 nm) for 3 m^2 façade. The artificially weathered lamellas were used for laboratory efficacy tests.

2.2 Laboratory efficacy tests

The laboratory efficacy tests were carried out with mold (Internal SOP 004'349), blue stain (EN 152:1988) and algae (Internal SOP 004'350) cultures on new specimens, 2 months naturally weathered specimens and artificially weathered specimens of all coatings except for ARwB. With ARwB, only new specimens and specimens after artificial weathering were tested. In each case, six specimens with dimensions of 40 × 40 × 10 mm^3 were tested for mold and algae, respectively, and for blue stain with dimensions 90 × 40 × 10 mm^3.

After weathering but before efficacy tests, all specimens were stored for 2 weeks under controlled climate conditions (20 °C, 65 % RH), then sterilized with ethylene oxide for 1 h under vacuum (0.65 bar, 55 °C) and finally placed in incubation vessels on Vermisol® Vermiculit. The pretreated specimens were inoculated with the microorganisms and incubated for 6 weeks (22 °C, 70 % RH) for mold and blue stain, respectively, and 12 weeks (room temperature and diffuse daylight) for algae. The rating factors are listed in Table 2. At the same time, growth and activity specimens were run additionally to control the vitality of the used microorganisms. More detailed information is given in Künniger et al. (2011).

3 Results and discussion

During the first year of natural weathering, only 8–24 l/m^2 rainwater, depending on the hydrophobic character of the coating, run over the coated surfaces of the façade elements. However, especially in spring and autumn, condensation also led to moisturisation of the façade promoting fungi and algae growth.

Already after 1 year, the OARwAg and HySi coatings as well as the untreated spruce specimens were affected by microorganisms, while the other coatings were still intact. The affection by microorganisms was delayed on the silane based coatings compared to uncoated spruce during outdoor weathering. It can be assumed that this effect was rather induced by the hydrophobicity of the coating and/or the silane components than by the Ag content, because the non-Ag formulation showed almost the same performance.

After 2 years of natural weathering, only the coatings with organic biocides (AARwB and ARwB) still remained unaffected. The silane based coatings with and without silver (HySiwAg and HySi) showed no difference and were comparable to the untreated spruce after 1 year of weathering.

Table 2 Efficacy tests; rating of non-weathered and weathered specimens
Tab. 2 Wirksamkeitstests; Bewertung von unbewitterten und bewitterten Proben

	Non-weathered	2 months natural weathering	Artificial weathering
Spruce[a]			
Mold	4	n.t.	n.t.
Blue stain	3	n.t.	n.t.
Algae	3	n.t.	n.t.
HySiwAg			
Mold	3.5	4.75	2.5
Blue stain	2.5	3.0	2.5
Algae	2.75	2.5	3.5
HySi			
Mold	4.5	5.0	4.0
Blue stain	2.5	3.0	2.5
Algae	2.5	2.5	2.75
OARwAg			
Mold	4.5	4.5	4.5
Blue stain	2.5	3.0	2.5
Algae	2.75	2.5	2.0
AARwB			
Mold	0.0	0.5	0.5
Blue stain	0.0	0.0	0.0
Algae	0.0	1.5	0.0
ARwB			
Mold	0.0	n.t.	0.0
Blue stain	0.0	n.t.	0.0
Algae	0.0	n.t.	0.0

Rating factors: Mold and algae: 0 Not affected, 1 Visible under microscope only, 2 Visible, ≤25 %**, 3 Visible, ≤50 %**, 4 Visible, >50 %**, 5 Visible, 100 %**

Blue stain: 0 Not affected, 1 Minor affected (max. 10 spots**, <2 mm), 2 Visible, ≤50 %**, 3 Visible, >50 %**

** Affected percentage of the tested specimen surface

[a] Untreated

Beside the low silver content in the coatings OARwAg and HySiwAg, there were some other reasons for the insufficient durability. The OARwAg coating showed a generally bad performance, also induced by insufficient UV protection. The early damaged coating could not protect the wood against moisture and established thereby a good basis for microorganism colonization. The silane based coating (HySiwAg) did not protect the wood substrate against air humidity and UV light. The UV degradation of the wood substrate underneath the coating led to a loss of the coating after a short time period. High wood moisture was a consequence and again the basis for microorganisms to grow.

Laboratory efficacy tests confirmed the observation results made on specimens during natural weathering. Only the two organic biocide containing coatings (AARwB and ARwB) showed sufficient protection against the tested microorganisms (Table 2).

The laboratory test clearly showed that a silver concentration below 50 ppm is not sufficient to protect the coating surface against microorganisms. Obviously, there are not enough silver ions freely available on the coating surface, which are necessary for an efficacy against fungi and algae. Free silver ions tend to react quickly with sulfur and/or chlorine compounds of the environment and are therefore no more effective against microorganisms. It has not yet been proven, whether a high initial silver content could overcome this problem.

4 Conclusion

The results of the study showed that under the tested conditions the silver containing commercial coatings did not protect a wooden façade against microorganisms such as mold, blue stain and algae. One reason for this result might have been the low initial silver concentration below 50 ppm in the coating.

A slightly delayed growth of microorganisms on the silane based coatings during natural weathering was rather induced by the hydrophobic character of the surface due to the silane components than by the silver content.

Acknowledgments Financial support of the Federal Office for the Environment (BAFU) and the 'Fonds zur Förderung der Wald-und Holzforschung' (WHFF) is gratefully acknowledged.

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