Effect of Surface Pretreatment with Natural Essential Oils on the Weathering Performance of Spruce Wood

Eliška Oberhofnerová,* Miloš Pánek, and Martin Böhm

The efficiency of surface pretreatment with natural essential oils relative to the weathering performance of Norway spruce wood was examined. This study investigated the combination of this pretreatment increasing biological resistance and oil-based coating with protection against ultraviolet light and hydrophobic topcoat with silicon nanoparticles during natural and artificial weathering. The coating systems were exposed to 24 months of natural weathering in climatic conditions of Central Europe and 2,016 hours of artificial weathering. The synergistic effect of a coating system based on safflower with essential oils and commercial oil-based coating was the most efficient. The application of one layer of an oil-based coating in a wet state of surface pretreatment exhibited results comparable to the application of two layers in a dry state. For all coating systems, increasing changes of colour, roughness, and surface wettability were observed, which differed according to the weathering method. Weathering performance of transparent coating systems was evaluated during both weathering tests by exact measurements, laser scanning microscopy and visual evaluation as well. Total colour difference did not prove to be a sufficient evaluation criterion to indicate coating performance during weathering.

Keywords: Essential oil; Hydrophobicity; Pretreatment; Spruce wood; Weathering

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INTRODUCTION

Norway spruce is traditionally the wood species most often used for construction applications in Central Europe. However, its lower natural durability against bio-attack (EN 350 2016) makes it unsuitable (Meyer-Veltrup *et al.* 2017) for application in severe environmental conditions (Van Acker *et al.* 2003) without any protection, as defined for Class 3-5 in EN 460 (1994) standard. When it is left unprotected and used as an exterior material, it loses its original properties and rapidly degrades *via* weather, fungi, bacteria, or insects. The degradation process caused by abiotic factors, such as solar radiation, water in all its states, temperature, wind, dust, or pollution (Temiz *et al.* 2005; Evans 2008), is called weathering. The surface is rapidly changed as well by moulds and wood-staining fungi action (Gobakken and Lebow 2010). Unlike decay or insect attack, weathering is typically not a significant factor in the failure of wood components and the collapse of a structure (Yildiz *et al.* 2011), but it can be a starting point for a decay (Buchner *et al.* 2018). Generally, weathering is mainly considered as an aesthetic phenomenon (Rüther 2011). It affects surface properties quickly, and as a result, unprotected wood changes colour to grey and acquires a typical rough structure (Feist 1992; Evans 2008; Gupta *et al.* 2011; Oberhofnerová *et al.* 2017). All wooden elements should respect the basic principles of construction design. Wood species with higher natural durability can be left unprotected in exterior applications, but species with lower natural durability, such as spruce, should be protected using the proper surface finish (Jones and Brischke 2017). The protective function of an exterior coating generally includes protection against moisture uptake and related dimensional changes, protection against photochemical degradation, and prevention of microbiological degradation (De Meijer 2001; Evans *et al.* 2015). However, coating systems themselves also undergo degradation caused by several weathering factors (Gobakken and Lebow 2010; Gaylarde *et al.* 2011; Grüll *et al.* 2011).

Extending the service life of wood and wood products using natural compounds as bioactives is proving to be an attractive approach for wood protection from the point of view of human health and environmental protection (Tomak et al. 2018). Not every natural compound can be regarded as eco-friendly. The use of all biocidal products is controlled by BPR regulation 528/2012 and requires an authorisation. To extend the service life of wood and maintain its natural look, transparent eco-friendly coating systems with minimal use of harmful chemicals are still at the center of attention (Pospíšil and Nešpurek 2000; Evans *et al.* 2015). Transparent finishes often contain ultraviolet light (UV) absorbers, stabilizers, biocides, and other additives, but their ability to protect wood from weathering is still limited (MacLeod *et al.* 1995; Pánek and Reinprecht 2014). Most of them fail within two years of exterior exposure (Evans *et al.* 2015).

Traditional wood protection methods employ chemicals that are considered toxic and can affect human health and environment, and there is a continuing dilemma concerning how to manage them at the end of their service life (Singh and Singh 2012). Although there are many ways to treat wood surfaces (Evans *et al.* 2015), multilayer coating systems using primers with commercial fungicides are currently the most-used variants of wood coating systems against weathering (Grüll *et al.* 2014b). Generally, there is an effort to use ecological surface treatments (Saha *et al.* 2011) with low volatile organic compound (VOC) content (De Meijer 2001; Miklečić *et al.* 2017) and to improve the performance of transparent coatings with improving modification agents. The effect of UV absorbers, stabilizers and nanoparticles is investigated in several studies (Evans 2008; Forsthuber and Grüll 2010; Ozgenc *et al.* 2012; Miklečić *et al.* 2017; Tomak *et al.* 2018). Hydrophobic coatings have been tested as a possible method to decrease the degradation of wood (Liu *et al.* 2013; Samyn *et al.* 2014; Žlahtič and Humar 2016). One way to increase durability of wood against biodegradation is the use of plant extractives or essential oils (Kartal *et al.* 2006; Nzokou and Kamdem 2006; Saha *et al.* 2011; Pánek *et al.* 2014) for surface pretreatment. The best efficiency has been found for those essential oils that contain phenolic compounds such as oregano, thyme, or clove (Lambert *et al.* 2001; Chittenden and Singh 2011; Pánek and Reinprecht 2014). They show promising protection against mould growth, but their interactions with coatings during the weathering process need to be investigated (Pánek *et al.* 2014; Reinprecht and Hulla 2015).

More qualitative parameters of wood coatings during exterior exposure can be evaluated (Grüll *et al.* 2011, 2014b; Žlahtič and Humar 2016). The change of colour during weathering serves as a basic indicator of the rate of weathering (Van den Bulcke *et al.* 2008; De Windt *et al.* 2014; Moya *et al.* 2017). The most effective protection against photoirradiation and discolouration is given by completely opaque pigmented coatings (De Meijer 2001; Reinprecht and Hulla 2015). In those applications, where wood remains visible, solar radiation will reach the wood surface and induce photochemical degradation of wood underneath the coating (MacLeod *et al.* 1995; De Meijer 2001).

A large percentage of coating degradation (paint defects, peeling, cracking, *etc.*) results from moisture changes in wood (Van Acker *et al.* 2014) and resulting effects on dimensional stability (Williams and Feist 1999; Gaylarde *et al.* 2011; Evans *et al.* 2015). The contact angle, which indicates the wettability by water on the exposed surfaces of coated wood, is an important indicator of the rate of weathering (Van den Bulcke *et al.* 2011; Žlahtič and Humar 2016). The permeability can both decrease (leaching of hydrophilic components) and increase in the initial stadium (formation of micro-cracks) during weathering (Derbyshire and Miller 1996; Oberhofnerová and Pánek 2016). The change in surface roughness and wettability during weathering has been discussed by previous researchers (Gardner *et al.* 1991; Gupta *et al.* 2011; Žlahtič and Humar 2016), but there is still a need to explore new protective treatments and test their durability. The achieved improvements of transparent coatings have not yet led to the development of a commercially affordable treatment that meets expectations of exterior durability (Evans *et al.* 2015; Miklečić *et al.* 2017).

The degradation of coatings on wood is revealed during service life (Grüll *et al.* 2011) or through natural (NW) and artificial weathering (AW) tests (Dawson *et al.* 2008; Van den Bulcke *et al.* 2008; Grüll *et al.* 2014b; Žlahtič and Humar 2016; Miklečić *et al.* 2017). Yet the methods differ greatly in achieved values of surface property changes (Grüll *et al.* 2014b; Reinprecht and Pánek 2015). Some studies have found no significant correlation between results obtained by natural and artificial weathering (Deflorian *et al.* 2008; Van den Bulcke *et al.* 2008; Moya *et al.* 2017). Laboratory artificial tests can accurately and rapidly predict the durability of coatings (Van den Bulcke *et al.* 2008; Reinprecht and Pánek 2015), but not all of the factors of weathering and moulding and staining can be recreated in an accelerated chamber (Grüll et al. 2014b). Thus the natural weathering should be used to verify the laboratory testing (Crewdson 2008; Grüll *et al.* 2014b).

The aim of this study was to evaluate the durability of different transparent coating systems applied on native or pretreated spruce wood during natural and artificial weathering. The combination of safflower oil, clove, and oregano essential oils was used as a surface pretreatment. Other coatings tested were the commercial oil-based coating with UV protection and the hydrophobic top coat on the base of silicon nanoparticles. Different combinations and layerings of these coatings were evaluated in this study. The efficiency of the coatings on the performance of wood was evaluated by confocal laser scanning microscopy and by measuring the discolouration, wettability, and roughness change.

EXPERIMENTAL

Materials

The experiment was conducted using Norway spruce wood (*Picea abies* L.) from the Central Bohemian Region with a mean density of 510 kg/m^3. Each group of coating systems was represented by 14 heartwood samples with the dimensions 375 mm × 78 mm × 20 mm (longitudinal x radial x tangential) for the natural weathering test and by 4 samples with the dimensions of 310 mm × 78 mm × 20 mm (longitudinal × radial × tangential) for the artificial weathering test. The samples were sanded with the sandpaper grit of 120, and the top ends were sealed by silicon to prevent water uptake. The samples were conditioned in laboratory conditions (20 ± 2 °C and 65% RH) before coating application and subsequently before each measurement.

Surface pretreatment and coating application

The surface pretreatment (the compound of essential oils – clove and oregano - in 5% solution of safflower oil), commercial oil-based paint UV OSMO 420 (Osmo Holz und Color GmbH & Co. KG, Warendorf, Germany), and the hydrophobic treatment based on silicon nanoparticles PMO 62 (HF Servis Ltd., Plešnice, Czech Republic) were applied by brush on the exposed radial surfaces of samples. The specifications and spreading rates based on producer recommendation are listed in Table 1. The list of transparent coating systems (A-F) with initial properties before weathering is given in Table 2.

Table 1. Specification and Spreading Rates of Used Treatments

Type	Designation	Effect	Specification	Spreading Rate
Surface pretreatment	Safflower oil + essential oils	Biological resistance	Clover and oregano in 5% solution of natural safflower oil	100 (g/m^2) in one layer
Base coat	UV OSMO 420	UV, biological and fungi resistance	Clear finish for exterior application, based on natural vegetable oils (sunflower and soybean oils) in dis-aromatized white spirit, Propiconazole as biocide, (benzene-free) with UV stabilizers	120 (g/m^2) in one layer
Top coat	PMO 62	Hydrophobicity, biological resistance	Nanoprotection based on silicon particles	80 (g/m^2) in one layer

Table 2. Coatings Systems (A-F) and their Initial Properties Before Weathering

Coat.	Surface Pretreatment	Base Coat	Top Coat	*L**	*a**	*b**	R_a (µm)	CA (°)
A	Safflower + essential oils (2)	-	-	78.28	6.16	28.05	4.91	113.19
B	Safflower + essential oils (2)	UV OSMO 420 (2)	-	74.53	7.82	36.72	1.52	96.42
C	Safflower + essential oils (2)	UV OSMO 420 (1*)	-	74.67	7.73	35.75	2.04	93.07
D	Safflower + essential oils (2)	-	PMO 62 (2)	78.10	6.15	28.18	4.61	110.9
E	-	UV OSMO 420 (2)	-	79.61	4.83	30.76	1.54	95.22
F	-	UV OSMO 420 (2)	PMO 62 (2)	79.99	4.62	31.19	1.71	94.06

Note: (x) indicates the number of layers, CA = contact angle, *L*a*b**, R_a, and CA are discussed in subsequent sections; * Indicates the application of the layer in the wet state of pretreatment

Natural Weathering (NW)

The NW test was performed at Suchdol, Prague (50° 07' 49.68'' N, 14° 22' 13.87'' E, elevation above sea level 285 m) and lasted 24 months from December 15, 2014, to December 15, 2016. The samples were exposed outdoors, at a 45 ° inclination, with radial surface facing south and placed approximately 1 m above the ground according to EN 927-3 (2006). At the 17th month of outdoor exposure, the samples were hit by hail approximately 3 cm in size. Overview of the climatic conditions during 24 months of weathering can be seen in Table 3.

Table 3. Overview of Climatic Conditions at the Test Site during the Exposure

Period (Months)	Average Temperature (°C)			Average Relative Humidity (%)			Total Precipitation in mm (number of rainy days)			Average Global Solar Radiation ($(kJ/m^2)/day$)	
	2015	2016		2015	2016		2015	2016		2015	2016
0 to 2	2.0	0.58		77.3	82.58		23.3 (21)	66.2 (34)		10678	11977
2 to 4	5.2	4.53		67.1	74.98		58.8 (27)	44.2 (25)		18722	18067
4 to 6	14.1	18.02		61.5	66.15		71 (27)	178.8 (29)		20488	20164
6 to 8	21.2	19.09		55.2	64.39		91.3 (21)	134 (31)		17432	16496
8 to 10	14.4	15.86		67.8	67.63		72.3 (22)	81.1 (23)		8496	5082
10 to 12	6.7	1.05		80.6	75.16		53.7 (28)	48 (22)		2549	2271
Note: Based on data from weather station (Meteostanice 2017)											

Artificial Weathering (AW)

The AW test was performed in laboratory using the QUV chamber with UVA fluorescent lamps (Q-Lab, Westlake, USA), which simulated exterior conditions according to EN 927-6 (2006). One cycle held for one week, which consisted of a condensation phase with a temperature of 45 °C (for 24 h) and the phases of UV radiation with the wavelength of λ = 340 nm and intensity of radiation 0.89 W/(m^2/nm) in the temperature of 60 °C (for 2.5 h) and water spraying with intensity of 6.5 L/min (for 0.5 h). The samples were cycled for 12 cycles (2016 h) under these conditions, which approximately corresponded to conditions during 24 months of natural weathering test (see above) based on the total UV irradiance during both weathering methods, as in the study of Fedor and Brennan (1996).

Methods

Colour Measurements

Colour parameters $L^*a^*b^*$ were determined according to the Commission International de l´Eclairage (CIE 1986) before weathering, and after 3 months, 6 months, 9 months, 12 months,18 months, and 24 months of NW, as well as after 168 h, 504 h, 1008 h, 1512 h, and 2016 h of AW. The colour characteristics were measured at the same measuring points (8 per sample) using a spectrophotometer 600d (Konica Minolta, Tokyo, Japan). The device was set to an observation angle of 10 °, d/8 geometry, and D65 light source. The total colour difference (ΔE) was calculated according using Eq. 1,

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

where L^* is the lightness from 100 (white) to 0 (black), a^* is the chromaticity coordinate from -60 (green) to + 60 (red), b^* is the other chromaticity coordinate from -60 (blue) to +60 (yellow), and ΔL^*, Δa^*, and Δb^* represent the differences between L^*, a^*, and b^* values before and after weathering.

Surface Wetting Measurements

The sessile drop method with static contact angle measurement (without external interference) was performed using the methodology of Bastani *et al.* (2015). The wettability measurements were taken using a goniometer Krüss DSA 30E device (Krüss, Hamburg, Germany) on radial surfaces of wood samples before weathering and after 3 months, 6 months, 9 months, 12 months, 18 months, and 24 months of NW as well as 2016 h of AW. Twenty measurements were taken for each sample, with distilled water drops with a dosing volume of 5 μL. The contact angle values were determined after 5 s of drop deposition. The phenomena of spreading and absorption of drops on the wood surface was investigated *via* variations of the weathering method, time, and coating system.

Surface Roughness Measurements

The surface roughness (arithmetic average of roughness value R_a) was determined according to ISO 4287 (1997) and ISO 4288 (1996) using a profilometer Talysurf Form Intra (Taylor-Hobson, Berwyn, USA). The measurements were taken in four traversing lengths oriented perpendicularly to the length of the samples over the radial surface before weathering and after 3 months, 6 months, 9 months, 12 months, 18 months, and 24 months of NW and 2016 h of AW.

Confocal Laser Scanning Microscopy and Visual Evaluation

To evaluate the surface degradation of coatings, the samples were regularly scanned using a Canon 2520 MFP scanner with 300 DPI resolution (Canon, Tokyo, Japan) and analysed using a confocal laser microscope Lext OLS4100 (Olympus, Tokyo, Japan). The cracks and degree of surface degradation were evaluated before and after weathering using both laser scanning microscopy and visual evaluation on the base of EN ISO 4628 (2003).

Statistical analysis

The statistical evaluation was performed with Statistica 12 software (Statsoft, Palo Alto, CA, USA) and MS Excel 2013 (Microsoft, Redmond, WA, USA) using mean values, standard deviations, analysis of variance (ANOVA), and the Tukey Unequal N HSD multiple comparison test.

RESULTS AND DISCUSSION

Colour Changes

In the ANOVA, the effect of coating system, weathering time, and their interaction on investigated properties (total colour difference, colour parameters, roughness, and contact angle value) was evaluated as statistically significant after both weathering tests ($p < 0.01$). Total colour difference (ΔE^*) indicated the coating durability during weathering, as stated in other studies (Van den Bulcke *et al.* 2008; De Windt *et al.* 2014; Moya *et al.* 2017). Using the multiple comparison test, the effect of surface pretreatment on the total colour difference value was evaluated as statistically insignificant after NW ($p = 0.98$), but as statistically significant after AW ($p < 0.01$) by comparing the coating systems (B) and (E).

Based on the graphs (Fig. 1), both weathering tests caused an increase of colour differences. High increases were noted during the initial part of weathering, which corresponded with other studies (Sharratt *et al.* 2009; Ozgenc *et al.* 2012; Reinprecht and Pánek 2015). However, during the next phase of NW, the discolouration due to the presence of mould, dirt, and dust in porous structure of wood was observed, corresponding with the study of Evans (2008) and Gaylarde *et al.* (2011). These factors caused a higher discolouration of coating systems (A) and (D) (based on safflower and essential oil mixture). The lower durability of these coatings had not been revealed during AW, for which all of the coatings reached similar total colour difference values (ΔE^*).

The overall changes of the total colour differences Δ*E** of coatings based on safflower and essential oils only, (A) and (D), were in the range 47 to 48 after NW and 23 to 24 after AW. For the rest of the coating systems, the changes of total colour difference were in the range of 11 to 13 after NW and 17 to 24 after AW.

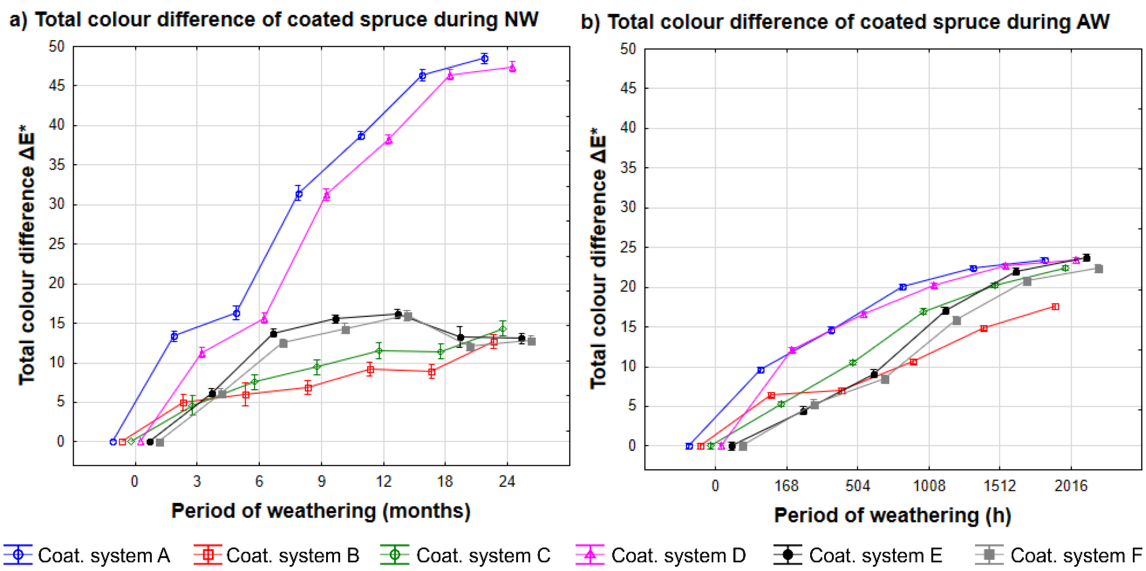

Fig. 1. Total colour difference of coated spruce wood during 24 months of natural weathering (a) and 2016 h of artificial weathering (b); ANOVA results representing the 95% confidence interval in vertical bars

Further investigation of colour parameters *L**, *a**, and *b** showed the differences between the durability of the tested coating systems. The statistically significant effect of surface pretreatment on the colour parameters *L**, *a**, and *b** had been observed after NW and AW ($p < 0.01$). Generally, the increase of values *a** and *b** shows a tendency for the surface to turn reddish and yellowish, respectively, and the increase of *L** indicates a tendency to turn into light colour (Temiz *et al.* 2005, 2007; Tolvaj and Mitsui 2005; Reinprecht and Pánek 2015). Based on the graphs (Fig. 2), the performance of UV-protective commercial oil-based coating systems (B, C, E, F) significantly differed from those coatings without this protection (A, D). All coating systems with UV protection layers (B, C, E, F) were characterized by decreased values of lightness, increased values of parameter *a**, and balanced values of parameter *b** during both weathering tests (Fig. 2), which corresponded well with the study of Baysal *et al.* (2014).

This result indicated that decomposed lignin (Teacă *et al.* 2013) and wood extractives (Pandey 2005) were protected against leaching by the protective coating layers. The coating systems based only on safflower with essential oils (A and D) acted differently. Both parameters *a** and *b** decreased during weathering, and lightness was the only exception (Fig. 2). The difference was caused by the presence of dust and moulds in the exterior (*L** value decrease), which pollute the degraded surface of wood (Evans 2008). This cannot be simulated in a UV chamber (Dawson *et al.* 2008; Ozgenc *et al.* 2012). Only the degradation of lignin and extractives, observed as initial decreased *L** values (Pandey 2005; Teacă *et al.* 2013), and their leaching by distilled water measured as increased *L** values (Sudiyani *et al.* 1999) was observed during AW (Fig. 2).

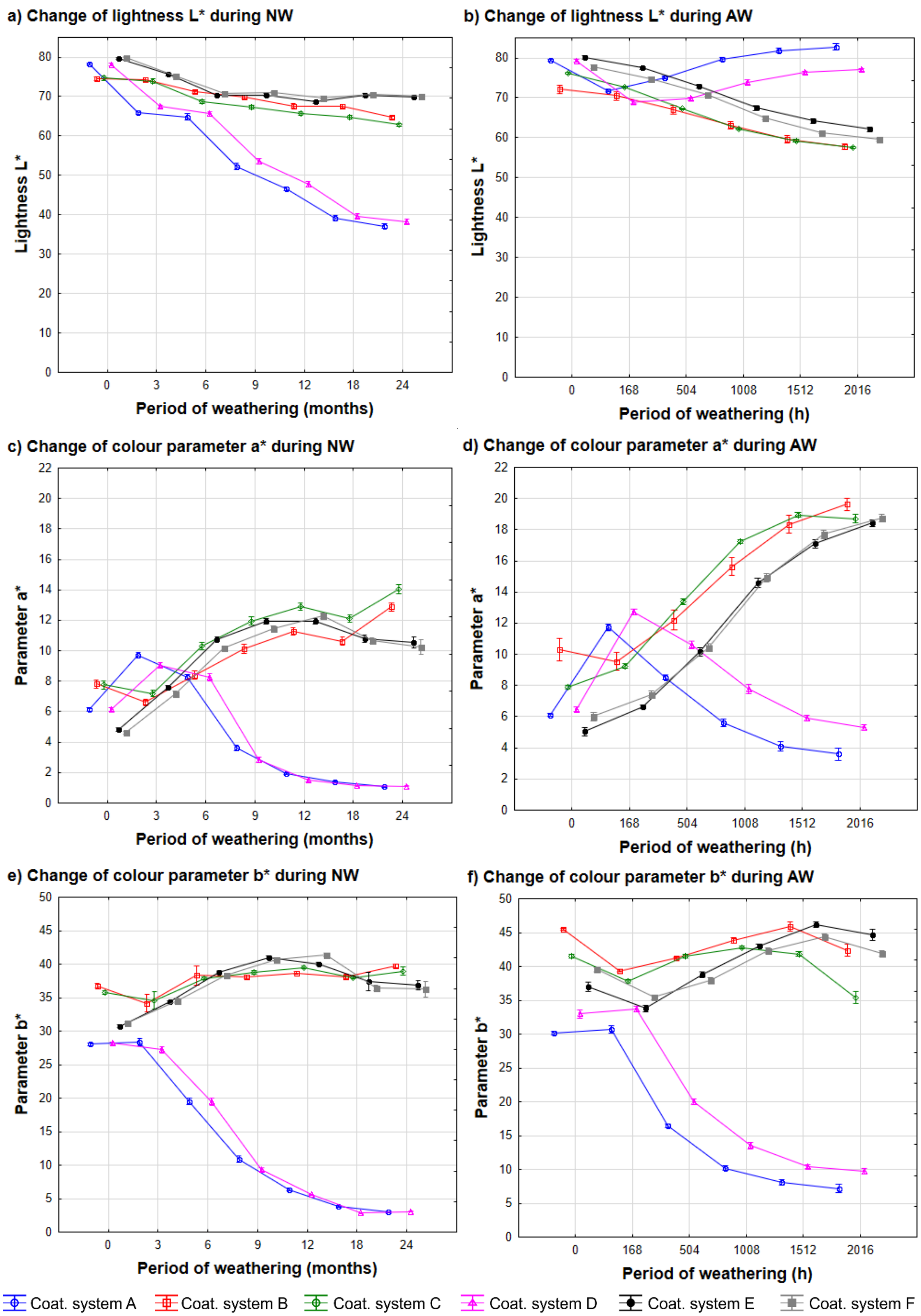

Fig. 2. Changes of colour parameters L*, a*, and b* of coated spruce wood during NW (a, c, and e) and AW (b, d, and f); ANOVA results representing the 95% confidence interval in vertical bars

Surface Roughness Changes

The surface roughness value R_a*, based on ISO 4287 (1997), was the second investigated parameter that indicated the performance of coating during weathering (Gardner *et al.* 1991; Gupta *et al.* 2011). The effect of coating system, weathering time, and their interaction on surface roughness was evaluated as statistically significant after NW and AW ($p < 0.01$). Based on the graphs (Fig. 3), the performance of the coating system based only on safflower and essential oils (A, D) differed from the rest of the coating systems (increasing roughness). There was no significant effect of surface pretreatment on the surface roughness during NW ($p = 1.00$) and AW ($p = 0.99$) when the coating systems (B) and (E) were compared using the multiple comparison test. The increased roughness indicated a lower coating durability (Yalcin and Ceylan 2017) and an advanced state of surface degradation, which became even more apparent after 18 months of NW, when the samples were hit by hail. The wood surfaces exposed to AW contained several cracks and splits, which was also observed in other studies (Temiz *et al.* 2005; Miklečić *et al.* 2017). The overall percentage changes of the surface roughness ΔR_a* of coatings (A) and (D) were in the range of 481 to 576 after NW and 292 to 427 after AW. For the rest of the coating systems, the percentage changes of surface roughness were in the range of 45 to 113 after NW and 21 to 95 after AW.

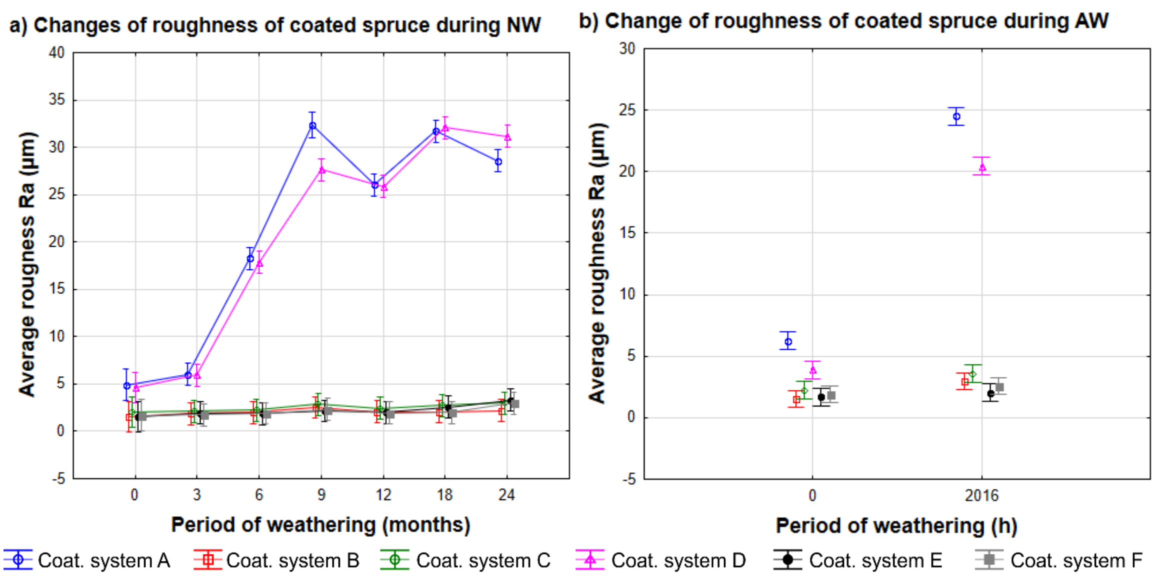

Fig. 3. Change of roughness of coated spruce wood during natural (a) and artificial weathering test (b); ANOVA results representing the 95% confidence interval in vertical bars

Surface Wettability Changes

The ANOVA showed the effect of the coating system, weathering time, and their interaction on the wettability as statistically significant after NW and AW ($p < 0.01$). The expected positive effect of the hydrophobic top layer on the surface wettability was observed only after its application, which was also recorded in studies of Liu *et al.* (2013) and Samyn *et al.* (2014). However, after NW and AW, there was no statistical significance ($p = 0.91$; $p = 0.90$, respectively), when comparing the coating systems (E) and (F) using the multiple comparison test. Based on the graphs (Fig. 4), the wettability of all the tested coating systems increased, *i.e.*, contact angle decreased, during both NW and AW, as in the study of Žlahtič and Humar (2016). The same trend of coating systems (A) and (D) was observed – the contact angle after exposure decreased to minimal values and the surface reached full wettability. The effect of surface pretreatment on the contact angle was noted as statistically significant after NW (p = 0.02) and insignificant after AW (p = 0.39) by comparing the coating systems (B) and (E). The rest of these coating systems were characterized by the similar decrease of contact angle during both weathering procedures. The overall percentage changes of the contact angle ΔCA* value of coatings (A) and (D) were approximately -100 % after NW and in the range of -100 to -91 after AW. For the rest of the coating systems, these percentage changes were in the range of -31 to 36 after NW and -57 to -46 after AW.

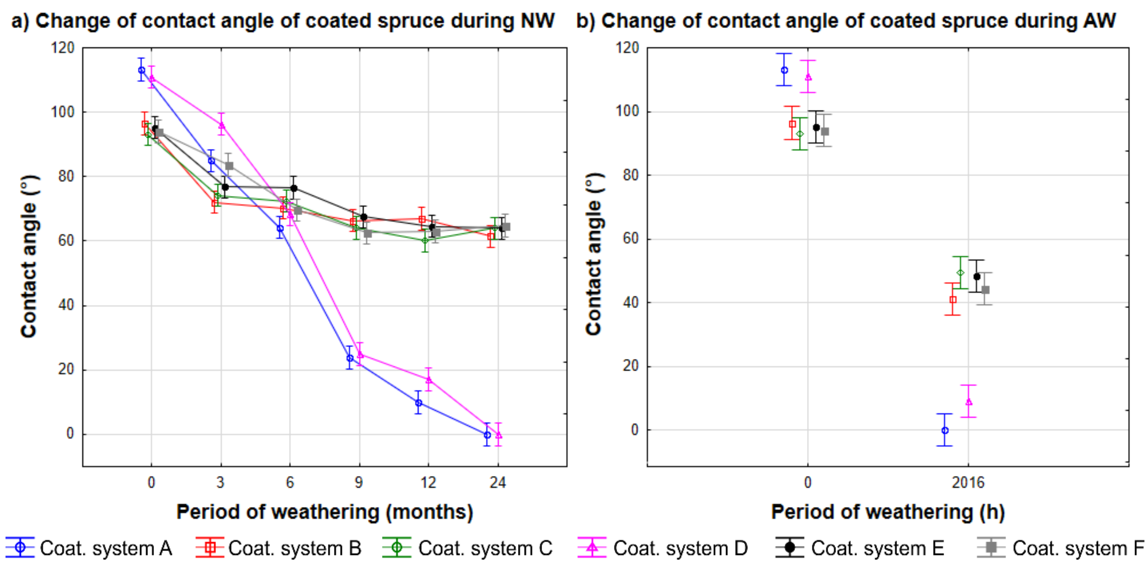

Fig. 4. Surface wettability, *i.e.* contact angle values, of coated spruce samples during natural (a) and artificial weathering (b); ANOVA results representing the 95% confidence interval in vertical bars

Visual Evaluation

The coating performance during NW was also evaluated visually in accordance with other studies (Grüll *et al.* 2011; De Windt *et al.* 2014). An initial visual inspection confirmed that weathering caused discolouration and degradation at natural outdoor and laboratory conditions as observed in other studies (Gupta *et al.* 2011; Pánek and Reinprecht 2014). The disruption of coating systems prevents the degradation of underlying wood (Evans 2015). The different performance of coating systems based only on pretreatment by safflower and essential oils (A, D) was visible already after 3 months of weathering when these samples became darker (Fig. 5). After 6 months of outdoor exposure, the samples were already grey with the beginning of mould growth, as in the study of Žlahtič and Humar (2016). After 18 months of weathering, the presence of mould on these coating systems had become obvious. The efficiency of essential oils layer only, as natural additives against biologic factors, proved to be low. They were leached from wood by water during exterior exposure (Pánek *et al.* 2014). During the 17th month of exposure, the samples were hit by hail, which caused mechanical damage of surface coatings that led to fungal staining, which was also recorded in the study of Uiterwaal and Blom (1973). The most affected were the coatings without the surface pretreatment (E and F), which showed degradation of disrupted coating in the form of greying, peeling, and formation of mould and fungi (Fig. 5). This was further investigated by confocal laser scanning microscopy (Fig. 6 and 7). Chalking was not considered because nonpigmented coatings were used (Dawson *et al.* 2008). The different performance of (A) and (D) coating systems in comparison with the rest of the systems is demonstrated in Fig. 5. More cracks were revealed during AW than NW (Grüll *et al.* 2014b; Miklečić *et al.* 2017), due to the shorter reaction time of wood to adapt to climatic changes and the associated dimensional changes during AW.

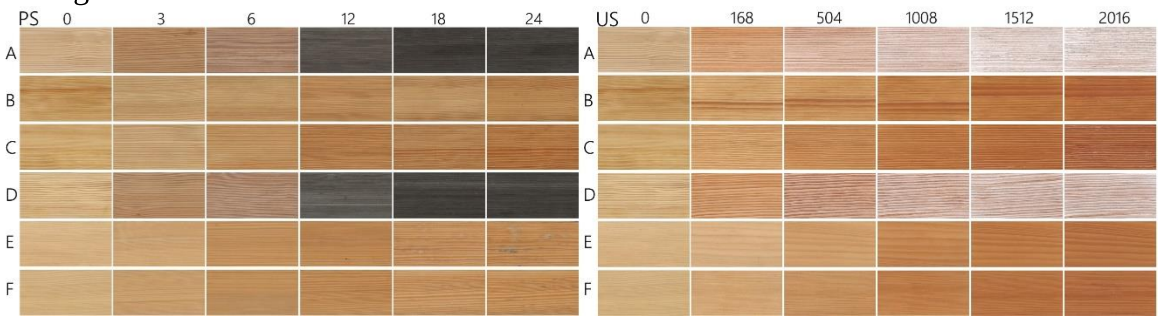

Fig. 5. The scans of coating systems (A-F) during natural weathering NW (0 months, 3 months, 6 months, 9 months, 12 months, 18 months, and 24 months) on the left and artificial weathering AW (0 h, 168 h, 504 h, 1008 h, 1512 h, and 2016 h) on the right, with the evaluation based on EN ISO 4628 (2003)

Laser scanning microscopy

For laser scanning microscopy, the representatives of coating system based on the pretreatment only (A) and commercial oil (E) after NW are shown in the Figs. 6 and 7.

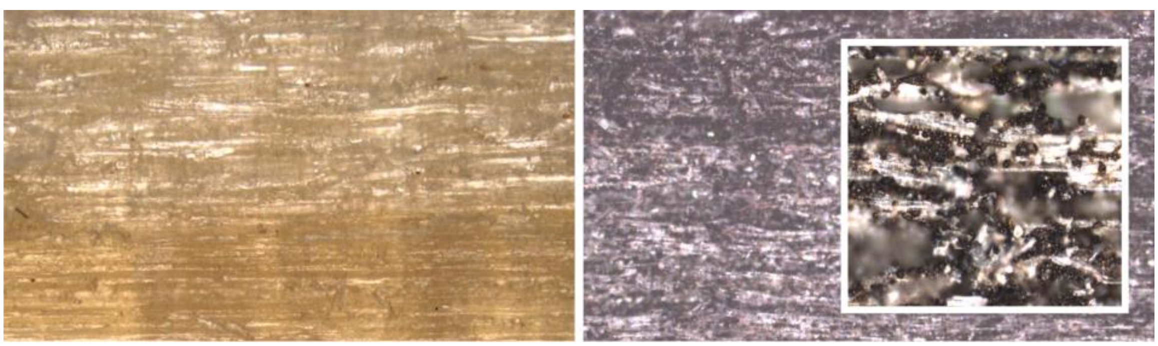

Fig. 6. Confocal laser scanning microscopy of coating system A before (left) and after 2 years of NW (right) with surface degradation detail

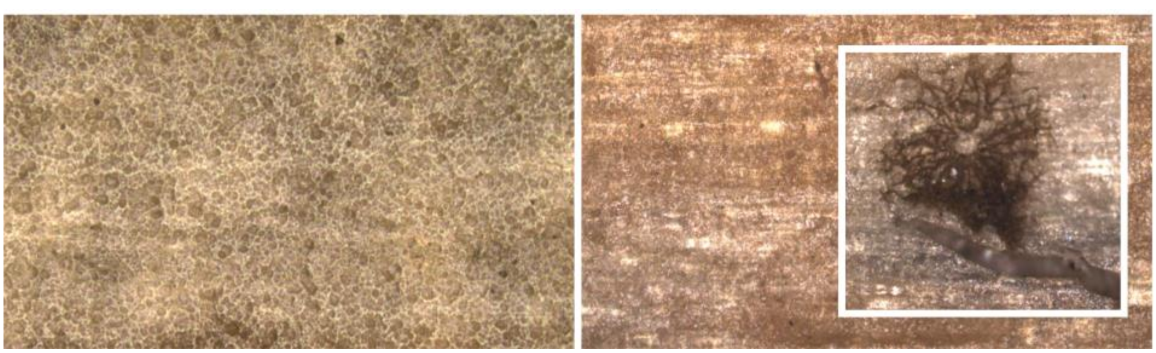

Fig. 7. Confocal laser scanning microscopy of coating system E before (left) and after 2 years of NW (right) with mould and fungi presence detail

In the case of coating system (A), the disruption of wood fibres, dirt, and the presence of moulds as a result of natural weathering was observed in detail (Fig. 6) (Evans 2008; Gobakken and Lebow 2010; Žlahtič and Humar 2016). The detail of coating system (E) after NW showed the area damaged by hail, where the mould and fungi began to form, similar to the study of Gaylarde *et al.* (2011). The synergistic effect of essential oils surface pretreatment and commercial oil (coating systems B and C) reached the best results, and moulds and fungi did not form on the bioprotected surface after getting hit by hail.

Final Discussion

To sum up the results, when comparing with previous work of Pánek and Reinprecht (2014), when only the oil-based coating was used (the same as type (E) in this study), this experiment illustrated a good synergistic effect of essential oils. This was also recorded in studies by Chittenden and Singh (2011) and Pánek *et al.* (2014). This was also true for the effect of coating systems on the biological resistance of coated spruce surfaces that was emphasized after being struck by hail during exposure. Results showed that using only a combination of safflower and essential oils was not effective enough, and degradation processes and surface changes of wood developed quickly due to their leaching by water from wood (Singh and Singh 2012; Pánek *et al.* 2014). Colour changes of coating (E) had similar trends as in the experiment by Pánek and Reinprecht (2014), but some differences in values of ΔE^* were observed and could be explained by local climatic differences (Creemers *et al.* 2002). In this experiment, the statistically significant effect of the oil-based commercial coating application on the wet state of surface pretreatment (essential and safflower oils) on the total colour difference ($p = 0.03$) was observed by comparing coating systems (B) and (C). The parameters L^* and a^* ($p < 0.01$) and contact angle ($p = 0.02$) after NW had significant effects on the total colour difference. In the case of AW, the parameters a^* and b^* ($p < 0.01$), the significant effect on the total colour difference was observed. Only one layer of this coating was sufficient for wood protection against weathering and fungal attack (Figs. 1 to 5), but as a disadvantage, the coating film had to be dried twice as long due to decreasing concentration of dis-aromatized white spirit after this application process. The effect of the hydrophobic layer based on silicone nanoparticles was observed only after its application. However, its degradation caused by weathering was very fast, and the prolongation of durability of tested coating systems was not observed (Figs. 1, 4, and 5). When comparing both experimental methods (NW and AW), the evaluation performed only at colour change basis was not sufficient enough, as was also stated in the studies of Grüll *et al.* (2014b), Reinprecht and Pánek (2015), and Moya *et al.* (2017). However, a combination of evaluating methods after AW also measuring the roughness changes and surface wettability created a satisfactory idea of quality and durability of the tested coatings along with a good assumption of their service life during natural weathering. Microscopic analyses of the coating clearly detected their degradation during exposure like in the studies of Masaryková *et al.* (2010) and Grüll *et al.* (2014a), without the need for preparation of special microscopic samples.

CONCLUSIONS

1. The interaction of essential oils and a safflower oil layer as a surface pretreatment of spruce wood in combination with top oil-based commercial coatings showed promise as a nontoxic variant of protection for exterior wood application with increased biological resistance.
2. The application of commercial oil in the wet state of an essential oil layer showed sufficient protection against weathering with a positive effect on the surface wettability.
3. The expected positive effect of the hydrophobic top layer PMO 62 on the surface wettability had not been demonstrated during exposure to both NW and AW.
4. The coating systems based on safflower and essential oils only, (A) and (D), showed a low ability to protect wood against weathering.
5. From the point of view of discolouration during weathering, the ΔE^* did not prove to be a sufficient evaluation criterion, which indicated that all of the colour parameters had to be investigated. Combination of other evaluating criteria was useful for better prediction of coatings service life when exposed outdoors.
6. The resulting values differed according to the testing method, but both the NW and AW methods revealed the specific durability of the tested coatings system, which was higher for the systems based on the UV protective commercial oil.

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REFERENCES CITED

Bastani, A., Adamopoulos, S., and Militz, H. (2015). "Water uptake and wetting behaviour of furfurylated, *N*-methylol melamine modified and heat-treated wood," *Eur. J. Wood Wood Prod.* 73(5), 627-634. DOI: 10.1007/s00107-015-0919-8

Baysal, E., Dizman Tomak, E., Ozbey, M., and Altin, E. (2014). "Surface properties of impregnated and varnished Scots pine wood after accelerated weathering," *Color. Technol.* 130(2), 140-146. DOI: 10.1111/cote.12070

Buchner, J., Irle, M., Belloncle, C., Michaud, F., and Macchioni, N. (2018). "Fungal and bacterial colonies growing on weathered wood surfaces," *Wood Mater. Sci. Eng.*, 1-9. DOI: 10.1080/17480272.2018.1443975

Chittenden, C., and Singh, T. (2011). "Antifungal activity of essential oils against wood degrading fungi and their applications as wood preservatives," *Int. Wood Prod. J.* 2(1), 44-48. DOI: 10.1179/2042645311Y.0000000004

Commission Internationale de l'Eclairage (CIE) (1986). *Colorimetry, 2nd Edition* (CIE Pub. No. 15.2), Commission Internationale de l'Eclairage, Vienna, Austria.

Creemers, J., De Meijer, M., Zimmermann, T., and Sell, J. (2002). "Influence of climatic factors on the weathering of coated wood," *Eur. J. Wood Wood Prod.* 60(6), 411-420. DOI: 10.1007/s00107-002-0338-5

Crewdson, M. (2008). "Outdoor weathering must verify accelerated testing," Q-Lab Weathering Research Service, 1005 SW 18th Avenue Homestead, FL 33034-1725 U.S.A (https://www.q-lab.com/documents/public/9d677625-3d76-47a0-8099-daf3b24290fc.pdf). Accessed 18th February 2018.

Dawson, B. S., Singh, A. P., Kroese, H. W., Schwitzer, M. A., Gallagher, S., Riddiough, S. J., and Wu, S. (2008). "Enhancing exterior performance of clear coatings through photostabilization of wood. Part 2: Coating and weathering performance," *J. Coat. Technol. Res.* 5(2), 207-219. DOI: 10.1007/s11998-008-9090-z

De Meijer, M. (2001). "Review on the durability of exterior wood coatings with reduced VOC-content," *Prog. Org. Coat.* 43(4), 217-225. DOI: 10.1016/S0300-9440(01)00170-9

De Windt, I., Van den Bulcke, J., Wuijtens, I., Coppens, H., and Van Acker, J. (2014). "Outdoor weathering performance parameters of exterior wood coating systems on tropical hardwood substrates," *Eur. J. Wood Wood Prod.* 72(2), 261-272. DOI: 10.1007/s00107-014-0779-7

Deflorian, F., Rossi, S., and Fedel, M. (2008). "Organic coatings degradation: Comparison between natural and artificial weathering," *Corros. Sci.* 50(8), 2360-2366. DOI: 10.1016/j.corsci.2008.06.009

Derbyshire, H., and Miller, E. R. (1996). "Moisture conditions in coated exterior wood. Part 1: An investigation of the moisture transmission characteristics of exterior wood coatings and the effect of weathering on coating permeability," *Journal of the Institute of Wood Science* 4(1), 40-47.

EN 350 (2016). "Durability of wood and wood-based products – Testing and classification of the durability to biological agents of wood and wood-based materials," European Committee for Standardization, Brussels, Belgium.

EN 460 (1994). "Durability of wood and wood-based products. Natural durability of solid wood. Guide to the durability requirements for wood to be used in hazard classes," European Committee for Standardization, Brussels, Belgium.

EN 927-3 (2006). "Paints and varnishes. Coating materials and coating system for exterior wood, Part 3: Natural weathering test," European Committee for Standardization, Brussels, Belgium.

EN 927-6 (2006). "Paints and varnishes. Coating materials and coating systems for exterior wood, Part 6: Exposure of wood coatings to artificial weathering using fluorescent UV lamps and water," European Committee for Standardization, Brussels, Belgium.

EN ISO 4628 (2003). "Paints and varnishes. Evaluation of degradation of coatings. Designation of quantity and size of defects, and of intensity of uniform changes in appearance," European Committee for Standardization, Brussels, Belgium.

Evans, P. D. (2008). "Weathering and photoprotection of wood," in: *Development of Commercial Wood Preservatives*, American Chemical Society, Washington, D.C., pp. 69-117. DOI: 10.1021/bk-2008-0982.ch005

Evans, P. D., Haase, J. G., Seman, A. S., and Kiguchi, M. (2015). "The search for durable exterior clear coatings for wood," *Coatings* 5(4), 830-864. DOI: 10.3390/coatings5040830

Fedor, G. R., and Brennan, P. J. (1996). "Comparison between natural weathering and fluorescent UV exposures: UVA-340 lamp test results," in: *STP16154S Durability Testing of Nonmetallic Materials*, R. Herling (ed.), ASTM International, West Conshohocken, PA, 91-105. DOI: 10.1520/STP16154S

Feist, W. C. (1992). "Natural weathering of wood and its control by water-repellent preservatives," *American Painting Contractor* 69(4), 18-25.

Forsthuber, B., and Grüll, G. (2010). "The effects of HALS in the prevention of photodegradation of acrylic clear topcoats and wooden surfaces," *Polym. Degrad. Stabil.* 95(5), 746-755. DOI: 10.1016/j.polymdegradstab.2010.02.016

Gardner, D. J., Generalla, N. C., Gunnells, D. W., and Wolcott, M. P. (1991). "Dynamic wettability of wood," *Langmuir* 7(11), 2498-2502. DOI: 10.1021/la00059a017

Gaylarde, C. C., Morton, L. H. G., Loh, K., and Shirakawa, M. A. (2011). "Biodeterioration of external architectural paint films – A review," *Int. Biodeter. Biodegr.* 65(8), 1189-1198. DOI: 10.1016/j.ibiod.2011.09.005

Gobakken, L. R., and Lebow, P. K. (2010). "Modelling mould growth on coated modified and unmodified wood substrates exposed outdoors," *Wood Sci. Technol.* 44(2), 315-333. DOI: 10.1007/s00226-009-0283-0

Grüll, G., Forsthuber, B., Tscherne, F., and Spitaler, I. (2014a). "Weathering indicator for artificial and natural weathering of wood coatings," *Eur. J. Wood Wood Prod.* 72(5), 681-684. DOI: 10.1007/s00107-014-0807-7

Grüll, G., Tscherne, F., Spitaler, I., and Forsthuber, B. (2014b). "Comparison of wood coating durability in natural weathering and artificial weathering using fluorescent UV-lamps and water," *Eur. J. Wood Wood Prod.* 72(3), 367-376. DOI: 10.1007/s00107-014-0791-y

Grüll, G., Truskaller, M., Podgorski, L., Bollmus, S., and Tscherne, F. (2011). "Maintenance procedures and definition of limit states for exterior wood coatings," *Eur. J. Wood Wood Prod.* 69(3), 443-450. DOI: 10.1007/s00107-010-0469-z

Gupta, B. S., Jelle, B. P., Jostein, H. P., and Rüther, P. (2011). "Studies of wooden cladding materials degradation by spectroscopy," *P. I. Civil. Eng- Constr. Mater.* 164(6), 329-340. DOI: 10.1680/coma.2011.164.6.329

ISO 4287 (1997). "Geometrical product specifications (GPS). Surface texture. Profile method. Terms, definitions and surface texture parameters," International Organization for Standardization, Geneva, Switzerland.

ISO 4288 (1996). "Geometrical product specifications (GPS). Surface texture. Profile method. Rules and procedures for the assessment of surface texture," International Organization for Standardization, Geneva, Switzerland.

Jones, D., and Brischke, C. (2017). *Performance of Bio-based Building Materials*, Woodhead Publishing Duxford, United Kingdom.

Kartal, S. N., Hwang, W.-J., Imamura, Y., and Sekine, Y. (2006). "Effect of essential oil compounds and plant extracts on decay and termite resistance of wood," *Holz. Roh. Werkst.* 64(6), 455-461. DOI: 10.1007/s00107-006-0098-8

Lambert, R. J. W., Skandamis, P. N., Coote, P. J., and Nychas, G.-J. E. (2001). "A study of the minimum inhibitory concentration and mode of action of oregano essential oil, thymol and carvacrol," *J. Appl. Microbiol.* 91(3), 453-462. DOI: 10.1046/j.1365-2672.2001.01428.x

Liu, F., Wang, S., Zhang, M., Ma, M., Wang, C., and Li, J. (2013). "Improvement of mechanical robustness of the superhydrophobic wood surface by coating PVA/SiO_2

composite polymer," *Appl. Surf. Sci.* 280, 686-692. DOI: 10.1016/j.apsusc.2013.05.043

MacLeod, I. T., Scully, A. D., Ghiggino, K. P., Ritchie, P. J. A., Paravagna, O. M., and Leary, B. (1995). "Photodegradation at the wood-clearcoat interface," *Wood Sci. Technol.* 29(3), 183-189. DOI: 10.1007/BF00204584

Masaryková, M., Pánek, M., and Reinprecht, L. (2010). "Micro-structural analysis of coatings with nanoscale particles after ageing in Xenotest," in: *Wood Structure and Properties '10*, J. Kúdela and R. Lagaňa (eds.), Arbora Publishers, Zvolen, Slovakia, pp. 209-216.

Meteostanice (2017). "Meteorological station of the Czech University of Life Sciences in Prague," Faculty of Agrobiology, Food and Natural Resources, (http://meteostanice.agrobiologie.cz), Accessed 4th Dec 2017.

Meyer-Veltrup, L., Brischke, C., Alfredsen, G., Humar, M., Flæte, P.-O., Isaksson, T., Brelid, P. L., Westin, M., and Jermer, J. (2017). "The combined effect of wetting ability and durability on outdoor performance of wood: Development and verification of a new prediction approach," *Wood Sci. Technol.* 51(3), 615-637. DOI: 10.1007/s00226-017-0893-x

Miklečić, J., Turkulin, H., and Jirouš-Rajković, V. (2017). "Weathering performance of surface of thermally modified wood finished with nanoparticles-modified waterborne polyacrylate coatings," *Appl. Surf. Sci.* 408, 103-109. DOI: 10.1016/j.apsusc.2017.03.011

Moya, R., Rodríguez-Zúñiga, A., Vega-Baudrit, J., and Puente-Urbina, A. (2017). "Effects of adding TiO_2 nanoparticles to a water-based varnish for wood applied to nine tropical woods of Costa Rica exposed to natural and accelerated weathering," *J. Coat. Technol. Res.* 14(1), 141-152. DOI: 10.1007/s11998-016-9848-7

Nzokou, P.,and Kamdem, D. (2006). "Influence of wood extractives on the photo-discoloration of wood surfaces exposed to artificial weathering," *Color Res. Appl.* 31(5), 425-434. DOI: 10.1002/col.20248

Oberhofnerová, E., and Pánek, M. (2016). "Surface wetting of selected wood species by water during initial stages of weathering," *Wood Res.* 61(4), 545-552.

Oberhofnerová, E., Pánek, M., and García-Cimarras, A. (2017). "The effect of natural weathering on untreated wood surface," *Maderas- Cienc. Tecnol.* 19(2), 173-184. DOI: 10.4067/S0718-221X2017005000015

Ozgenc, O., Hiziroglu, S., and Yildiz, U. C. (2012). "Weathering properties of wood species treated with different coating applications," *BioResources* 7(4), 4875-4888. DOI: 10.15376/biores.7.4.4875-4888

Pandey, K. K. (2005). "A note on the influence of extractives on the photo-discoloration and photo-degradation of wood," *Polym. Degrad. Stabil.* 87(2), 375-379. DOI: 10.1016/j.polymdegradstab.2004.09.007

Pánek, M., and Reinprecht, L. (2014). "Colour stability and surface defects of naturally aged wood treated with transparent paints for exterior constructions," *Wood Res.* 59(3), 421-430.

Pánek, M., Reinprecht, L., and Hulla, M. (2014). "Ten essential oils for beech wood protection—Efficacy against wood-destroying fungi and moulds, and effect on wood discoloration," *BioResources* 9(3), 5588-5603. DOI: 10.15376/biores.9.3.5588-5603

Pospíšil, J., and Nešpurek, S. (2000). "Photostabilization of coatings. Mechanisms and performance," *Prog. Polym. Sci.* 25(9), 1261-1335. DOI: 10.1016/S0079-6700(00)00029-0

Reinprecht, L., and Hulla, M. (2015). "Colour changes of beech wood modified with essential oils due to fungal and ageing-fungal attacks with *Coniophora puteana*," *Drewno* [*Wood*] 58(194), 37-48. DOI: 10.12841/wood.1644-3985.114.03

Reinprecht, L., and Pánek, M. (2015). "Effects of wood roughness, light pigments, and water repellent on the color stability of painted spruce subjected to natural and accelerated weathering," *BioResources* 10(4), 7203-7219. DOI: 10.15376/biores.10.4.7203-7219

Rüther, P. (2011). "Wood weathering from a service life perspective," Dissertation, Norwegian University of Science and Technology, Trondheim.

Saha, S., Kocaefe, D., Boluk, Y., and Pichette, A. (2011). "Enhancing exterior durability of jack pine by photo-stabilization of acrylic polyurethane coating using bark extract. Part 1: Effect of UV on color change and ATR–FT-IR analysis," *Prog. Org. Coat.* 70(4), 376-382. DOI: 10.1016/j.porgcoat.2010.09.034

Samyn, P., Stanssens, D., Paredes, A., and Becker, G. (2014). "Performance of organic nanoparticle coatings for hydrophobization of hardwood surfaces," *J. Coat. Technol. Res.* 11(3), 461-471. DOI: 10.1007/s11998-014-9576-9

Sharratt, V., Hill, C. A. S., and Kint, D. P. R. (2009). "A study of early colour change due to simulated accelerated sunlight exposure in Scots pine (*Pinus sylvestris*)," *Polym. Degrad. Stabil.* 94(9), 1589-1594. DOI: 10.1016/j.polymdegradstab.2009.04.010

Sudiyani, Y., Tsujiyama, S., Imamura, Y., Takahashi, M., Minato, K., and Kajita, H. (1999). "Chemical characteristics of surfaces of hardwood and softwood deteriorated by weathering," *J. Wood Sci.* 45(4), 348-353. DOI: 10.1007/BF00833502

Teacă, C. A, Roşu, D., Bodîrlău, R., and Roşu, L. (2013). "Structural changes in wood under artificial UV light irradiation determined by FTIR spectroscopy and color measurements – A brief review," *BioResources* 8(1), 1478-1507. DOI: 10.15376/biores.8.1.1478-1507

Temiz, A., Terziev, N., Eikenes, M., and Hafren, J. (2007). "Effect of accelerated weathering on surface chemistry of modified wood," *Appl. Surf. Sci.* 253(12), 5355-5362. DOI: 10.1016/j.apsusc.2006.12.005

Temiz, A., Yildiz, U. C., Aydin, I., Eikenes, M., Alfredsen, G., and Çolakoglu, G. (2005). "Surface roughness and color characteristics of wood treated with preservatives after accelerated weathering test," *Appl. Surf. Sci.* 250(1-4), 35-42. DOI: 10.1016/j.apsusc.2004.12.019

Tolvaj, L., and Mitsui, K. (2005). "Light source dependence of the photodegradation of wood," *J. Wood Sci.* 51(5), 468-473. DOI: 10.1007/s10086-004-0693-4

Tomak, E. D., Yazici, O. A., Parmak, E. D. S., and Gonultas, O. (2018). "Influence of tannin containing coatings on weathering resistance of wood: Combination with zinc and cerium oxide nanoparticles," *Polym. Degrad. Stabil.* 152, 289-296. DOI: 10.1016/j.polymdegradstab.2018.03.012

Uiterwaal, D. J. D., and Blom, C. W. (1973). "Role of coatings in timber preservation," in: *Proceedings of the Record Annual Convention British Wood Preserves Association*, Cambridge, UK, pp. 2-5.

Van Acker, J., De Windt, I., Li, W., and Van den Bulcke, J. (2014). "Critical parameters on moisture dynamics in relation to time of wetness as factor in service life prediction," in: Proceedings of *45th Annual Meeting of the International Research Group on Wood Protection*, St. George, UT, USA, Document IRG/WP 14-20555 pp. 22.

Van Acker, J., Stevens, M., Carey, J., Sierra-Alvarez, R., Militz, H., Le Bayon, I., Kleist, G., and Peek, R. D. (2003). "Biological durability of wood in relation to end-use. Part 1. Towards a European standard for laboratory testing of the biological durability of wood," *Holz. Roh. Werkst.* 61(1), 35-45. DOI: 10.1007/s00107-002-0351-8

Van den Bulcke, J., De Windt, I., Defoirdt, N., De Smet, J., and Van Acker, J. (2011). "Moisture dynamics and fungal susceptibility of plywood," *Int. Biodeter. Biodegr.* 65(5), 708-716. DOI: 10.1016/j.ibiod.2010.12.015

Van den Bulcke, J., Van Acker, J., and Stevens, M. (2008). "Experimental and theoretical behavior of exterior wood coatings subjected to artificial weathering," *J. Coat. Technol. Res.* 5(2), 221-231. DOI: 10.1007/s11998-007-9074-4

Williams, R. S., and Feist, W. C. (1999). *Water Repellents and Water-repellent Preservatives for Wood* (FPL-GTR-109), U.S. Department of Agriculture Forest Products Laboratory, Madison, WI. DOI: 10.2737/FPL-GTR-109

Yalcin, M., and Ceylan, H. (2017). "The effects of tannins on adhesion strength and surface roughness of varnished wood after accelerated weathering," *J. Coat. Technol. Res.* 14(1), 185-193. DOI: 10.1007/s11998-016-9841-1

Yildiz, S., Yildiz, U. C., and Tomak, E. D. (2011). "The effects of natural weathering on the properties of heat-treated alder wood," *BioResources* 6(3), 2504-2521. DOI: 10.15376/biores.6.3.2504-2521

Žlahtič, M., and Humar, M. (2016). "Influence of artificial and natural weathering on the hydrophobicity and surface properties of wood," *BioResources* 11(2), 4964-4989. DOI: 10.15376/biores.11.2.4964-4989

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