Influence of Artificial and Natural Weathering on the Hydrophobicity and Surface Properties of Wood

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The use of wood in outdoor, above-ground applications is increasing in Europe. To further increase wood usage, more information related to service life and maintenance costs must be provided. Water exclusion efficacy (WEE) is one of the most important factors influencing service life and strongly correlates to wood moisture dynamics, surface properties, and hydrophobicity (WEE as a whole). WEE can be improved with modifications and hydrophobic treatments. The aim of this study was to elucidate which wood surface properties affect WEE and to note changes over time caused by artificial or natural aging. Wood samples of oak (*Quercus*), sweet chestnut (*Castanea sativa*), European larch (*Larix decidua*), Scots pine heartwood and sapwood (*Pinus sylvestris*), Norway spruce (*Picea abies*), and beech (*Fagus sylvatica*) were used to investigate this phenomenon. The moisture performance of the wood samples was improved with thermal modification, wax, oil, and biocide treatment. In total, 17 materials were prepared. After treatment, four different aging procedures were applied. Before and after aging, Fourier transform infrared spectra, colour, and contact angle were determined. The analysis of untreated wood based materials indicated that durability and hydrophobicity are related. Of all the treatments, wax performed the best and retained high hydrophobicity even after the most severe aging method (outdoor exposure).

Keywords: Wood; Thermal modification; Hydrophobic treatment; Wax; Oil; Aging; Water; Contact angle; Colour

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INTRODUCTION

In addition to having a variety of indoor applications, wood has been used for centuries for structural and other outdoor applications. In recent years, Europe has seen a renaissance of the use of wood in construction applications. Its use especially in Class 2 (outside, not in ground contact, covered) and Class 3 (outside, not in ground contact, not covered) applications, as defined by EN 335 (2013), have become increasingly important. The use of less durable wood in higher-moisture applications has been enabled by the development of a new generation of wood-based materials, such as modified wood, hybrids, and composites. However, if wood is misused, it is susceptible to degradation, especially by fungi (Brischke and Thelandersson 2014). In nature, this is an important and desirable process, but for engineers and end users, wood degradation is one of its critical weaknesses. One of the biggest threats to outdoor wooden applications in Central Europe is wood-decaying fungi (Brischke and Rapp 2008). There are several research methods used to determine when decay occurs and how long a certain construction will last. This information refers to the service life of wood and is key data for planning service and

maintenance costs. Service life planning considers the extension of the service life of wood through the proper design of details, selection of wood, and wood preservation or modification (Brischke *et al*. 2006).

The service life of wood, defined in the standard ISO 15686-1 (2000) as the "period of time after installation during which a building or its parts meets the performance requirements," is specifiable in years. The service life of wood depends on both natural and improved durability. In the past, natural durability was linked to extractive components, the anatomical and chemical properties of the wood, and the presence of biocidal active ingredients. To a lesser extent, cell wall structure and wood density were also considered (Brischke *et al*. 2006). There are only a few naturally durable wood species available in Europe. According to standard EN 350 (2015), the majority of wood species in Central Europe have non-durable or susceptible wood. To use these wood species in relatively damp applications, their durability must be improved with proper treatment. Various biocidal preservatives with toxic ingredients have been used for impregnation, or a naturally durable tropical wood was used. Environmental concerns have resulted in renewed interest in non-biocidal solutions for wood protection, such as water repellents (Ghosh *et al*. 2008; Lesar *et al*. 2011b; Li *et al.* 2015). Recent improvement methods are designed differently than classical biocides. The purpose of biocides is to kill pests, while state-of-the-art methods are based on non-toxic mechanisms. They change the structure of the wood so that pests do not recognize it as a food source (Tjeerdsma *et al*. 1998; Esteves and Pereira 2009), or the wood moisture content is kept so low that decay is no longer possible (Goethals and Stevens 1994; Lesar and Humar 2010).

For end users of wooden applications, it is very important to predict the service life of wood. Different approaches for service life prediction have been developed, including the factor method (ISO 15686-1 2000). This method calculates the estimated service life (ESL) by multiplying a reference service life (RSL) with different modifying factors (Brischke *et al*. 2006). This method and recent results reflect the importance of moisture dynamics in evaluating the overall performance of naturally durable wood species and modified wood in outdoor applications (Rapp *et al*. 2000; Van den Bulcke *et al*. 2011). This phenomenon is frequently described as the water exclusion efficacy (WEE). The importance of moisture dynamics in wood performance scenarios has influenced the development of new European standards EN 350 (2015) and EN 16818 (2015).

WEE is therefore one of the most important factors influencing the performance of wooden structures in above-ground applications. Furthermore, it clearly indicates susceptibility against wood decay fungi. It strongly correlates with the moisture dynamics of wood and its hydrophobicity. The moisture dynamic of wood is affected by several interrelated wood properties: surface properties, capillary properties, and sorption characteristics (Van den Bulcke *et al*. 2011). Some naturally durable wood species exhibit these properties by themselves. However, hydrophobicity and consequently, WEE, can be improved with certain modifications (Hill 2011) and hydrophobic treatments such as waxes or oils (Humar and Lesar 2013; Humar *et al*. 2014; Lozhechnikova *et al*. 2015), but this phenomenon is not yet fully understood. Cited data clearly indicates that service life of wood can be considerably prolonged with wax and oil treatment. In general, impregnation with oils was found to be more effective towards wood decay fungi than impregnation with waxes. However, after six to ten months of exposure of oil treated wood in outdoor applications, the surface of oil-treated wood looks ugly, due to micro-organisms growing on the surface of oil-treated wood. On the other hand, wax treated wood become silver grey, what makes him very attractive for decking applications. Among various tested

waxes, fossil waxes from coal performed the best, presumably because they form thin layer of hard film and higher melting point than the majority of commercial waxes.

The majority of research on WEE and hydrophobicity has been performed on fresh, non-weathered samples or soon after application of hydrophobic treatments. These data are less relevant, since this state represents wood in the first months of exposure only. Latter one, wood is exposed to weathering and various type of degradation. Since the desired service life of wood is several decades, it is of considerable importance to determine changes in the moisture dynamics of wood caused by biotic (blue stain fungi, wood degradation fungi) and abiotic (UV) factors of degradation. This paper elucidates the surface properties of wood that affect WEE and showed changes over time caused by artificial or natural aging. We believe that performance of weathered wood is much more representative for real case scenario than freshly treated wood.

EXPERIMENTAL

Materials

The wood species chosen for this study are important in Central Europe, namely, oak heartwood (*Quercus*), sweet chestnut heartwood (*Castanea sativa*), European larch heartwood (*Larix decidua*), Scots pine heartwood and sapwood (*Pinus sylvestris*), Norway spruce heartwood (*Picea abies*), and beech (*Fagus sylvatica*) wood (Table 1). Scots pine and beech were chosen as they are standard low performing wood material in Europe. Norway spruce was included, as spruce is the most important wood species for construction applications in Europe. The performance of spruce wood is much better than that of the pine sapwood, presumably due to the better water exclusion efficacy. Larch wood, on the other hand, is one of the first choices for architects for decking applications in Central Europe. English oak was included as one of the commercially important more durable species, and sweet chestnut served as control. Sweet chestnut has similar anatomical structure than oak (ring porous wood), but better durability than oak. Specimens were defect-free, without visible signs of decay or blue staining, as prescribed in standard EN 113 (2006). The dimensions of the specimens were 1.5 cm × 2.5 cm × 5.0 cm. Some of the materials were subsequently treated with various solutions or thermally modified. The materials were classified into various durability classes as prescribed in standard EN 350 (2015). Oak and sweet chestnut are durable species (2nd class), and heartwood of European larch and Scots pine are moderately durable species (3rd class). Norway spruce was classified as less durable (4th class), and beech and Scots pine sapwood were classified as non-durable species (5th class).

Treatment of specimens

Some materials (Table 1) were treated with commercial treatments frequently used for joinery, garden furniture, decking, and other outdoor applications. Seventeen different materials were prepared for this experiment. In total, 1020 specimens were prepared, including five parallel specimens for each material and aging test and 10 control specimens (60 specimens for one material).

Thermal modification was performed according to the commercial Silvapro® process (Rep *et al*. 2012). This process is characterized by vacuum in the first step. Modification of the wood was performed for 3 h at 230 °C for Norway spruce and at 215 °C for beech wood. The entire process took 24 h. Process was controlled through the

temperature sensors mounded inside the small specimens, thus potential burning of the specimens was prevented. After modification, the specimens were conditioned for four weeks under laboratory conditions (T = 23°C; RH = 65%).

In order to upgrade the wood properties (durability, hydrophobicity), wood samples (Table 1) were treated with various solutions including (1) a 10% natural wax suspension mixed with distilled water (Lesar *et al*. 2011a); (2) tung oil (Humar and Lesar 2013); and (3) commercial copper-ethanolamine formulation (CuEA) (Silvanolin, Silvaprodukt), which contains five ingredients: copper(II) hydroxide, ethanolamine, quaternary ammonium compound, octanoic acid, and boric acid (Humar and Lesar 2008). The concentration of active ingredients and consequent retention conformed to the Class 3 requirements (above ground and uncovered (EN 335 2013)). Wax emulsion and tung oil were chosen to improve the hydrophobic properties of wood, while copper-ethanolamine treatment was used to improve the fungicidal properties of less durable wood.

Impregnation with all treatment solutions was performed according to the full cell process, *i.e*., 30 min vacuum (80 mbar), 120 min pressure (8 bar), 15 min vacuum (80 mbar), and 20 min soaking. Uptake of the treatment solutions was determined gravimetrically. Specimens were conditioned for four weeks after impregnation; the first two weeks in closed chambers, the third week in a half-open chamber, and the fourth week in an open chamber.

Aging Procedures

Four different standardized and non-standardized aging procedures were applied, with two different exposure times. A list of aging procedures with abbreviations is given in Table 2. Prior to and after all aging procedures, conditioned specimens were oven-dried at 103 ± 2 °C to a constant mass and weighed to determine the oven-dry mass.

Incipient fungal decay

Incipient fungal decay is usually not clearly visible. The first signs of decay on susceptible wood materials are observed within the first year of exposure. However, this decay is usually limited, although it can lead to considerable changes in the wood (Highley 1999). It is presumed, that if fungi make wood more permeable, its hydrophobicity and WEE are decreased. The first set of specimens were therefore exposed to fungi according to the modified EN 113 standard procedure (2006).

Conditioned specimens were steam-sterilized in an autoclave before exposure to wood decay fungi; 350-mL experimental glass jars with aluminium covers and cotton wool with 50 mL of 4% potato dextrose agar (DIFCO) were prepared and inoculated with brown rot (*Gloeophyllum trabeum*, or Gt2) or white rot fungi (*Schizophyllum commune*, or Scc). Both fungal isolates were obtained from the Collection of Microorganisms of the Biotechnical Faculty of the University of Ljubljana, Slovenia. The appropriate fungi were selected on the basis of their appearance as the first fungi on wood on the field test site in Ljubljana (Lesar and Humar 2010).

One week after inoculation, specimens were positioned on a plastic HDPE mesh, which was used to avoid direct contact between the samples and the medium (Thaler *et al*. 2014). There were five replicate samples used for two different exposures (one month (A) and two months (B)) for both fungi. The assembled test glasses were then incubated at 25 °C and 80% relative humidity (RH). After exposure, the fungal mycelium was removed, and the specimens were isolated.

Table 1. Materials and Treatment Solutions Used

Wood species	Scientific Name	Treatment Solutions					Abbreviations
		Wood	Thermal Modification	Impregnation with Cu Ethanolamine Preservative	Impregnation with Montan Wax Emulsion	Impregnation with Tung Oil	
Oak	*Quercus*	x					*Q*
Sweet Chestnut	*Castanea sativa*	x					*Cs*
European Larch	*Larix decidua*	x					*Ld*
		x				x	*LdOl*
Scots Pine (Heartwood)	*Pinus sylvestris*	x					*PsH*
Norway Spruce	*Picea abies*	x					*Pa*
		x	x				*PaTm*
		x		x			*PaCu*
		x	x	x			*PaTmCu*
		x			x		*PaWa*
		x				x	*PaOl*
		x	x		x		*PaTmWa*
		x	x			x	*PaTmOl*
Beech	*Fagus sylvatica*	x					*Fs*
		x	x				*FsTm*
		x	x		x		*FsTmWa*
Scots Pine (Sapwood)	*Pinus sylvestris*	x					*PsS*

Blue staining fungi

Blue staining fungi are usually the first colonizers of a wooden surface. Blue staining appears fairly rapidly. If the moisture conditions are favourable, blue staining develops within the first few weeks of exposure. One set of specimens were exposed to the blue stain fungi *Aureobasidium pullulans* and *Sclerophoma pithyophila*. Both fungal strains are standard organisms that infest most wooden commodities. *Aureobasidium pullulans* in particular disfigures wood coatings and exposed timber (Sharpe and Dickinson 1992). Exposure to blue stain fungi was performed as prescribed by the EN 152-1 protocol (1996). A liquid nutrient medium with malt agar and blue stain fungi spores was prepared and incubated in a fungal growth chamber for 4 days. The specimens were submerged in a mixed spore suspension prior to exposure and afterwards transferred to experimental jars (350 mL) containing 15 mL of spore suspension. The incubation (25 °C; 80% RH) times were the same as for fungal exposure: one month (Blue SF-A) and two months (Blue SF-B). After exposure, specimens were isolated, cleaned of mycelia, and dried.

Artificially accelerated weathering

Artificially accelerated weathering (AWW) was carried out in a chamber (ATLAS UP, Suntest XXL+, Linsengericht, Germany) that was set at the most severe typical exterior conditions, as recommended by EN/ISO 11341 (2005). This exposure simulates outdoor weathering without the contribution of biotic factors. UV radiation is so harsh that there is no fungal growth. The specimens were exposed to a controlled climatic air temperature of 38 °C and a relative humidity of 68% with UV radiation (0.35 W/m^2) and artificial rain for 1000 h in alternating cycles. One cycle of AAW lasted for 120 min and consisted of water spray (18 min) and UV radiation (102 min). In total, 1000 h of exposure reflects 1,260,000 KJ/m^2 received energy, which is comparable to six months of outdoor weathering.

Table 2. List of the Aging Procedures and Abbreviations

Aging Procedure	Time of Exposure	Abbreviations
Non-aged	/	Non-aged
Fungal decay—*Gloeophyllum trabeum*	1 month	Gt2-A
Fungal decay—*Gloeophyllum trabeum*	2 months	Gt2-B
Fungal decay—*Schizophyllum commune*	1 month	Scc-A
Fungal decay—*Schizophyllum commune*	2 months	Scc-B
Blue staining fungi	1 month	Blue SF-A
Blue staining fungi	2 months	Blue SF-B
Artificially accelerated weathering	1000 hours	AAW
Outdoor aging	9 months	OutDW-A
Outdoor aging	18 months	OutDW-B

Outdoor aging

Additional specimens were exposed to outdoor weathering in the field test site of the Department of Wood Science and Technology, Biotechnical Faculty, Ljubljana, Slovenia (N 46°02'55.4", E 14°28'44.6", 300 m above sea level). The first set of exposed material (OutDW-A) remained outside from January 2014 to October 2014. The average temperature during the exposure time was 12.6 °C, the average relative humidity was 78%, and the total precipitation was 1850.5 mm, with 184 rainy days (ARSO 2015). The second

set of material (OutDW-B) was aged for 18 months, from January 2014 until August 2015. The average temperature during the exposure time was 12.5 °C, the average relative humidity was 75%, and the total precipitation was 2,519 mm, with 261 rainy days (ARSO 2015).

Wood Characterization

Mass change

After exposure to different aging procedures, specimens were oven-dried at 103 ± 2 °C to a constant mass and weighed to determine the oven-dry mass (Sartorius, Germany). Accuracy of the balance was 0.0001 g. The mass change was then calculated. In the second step, the influence of aging on the surface properties and moisture dynamics of the wood was determined. Prior to contact angle measurement, colour and FTIR analysis, all specimens were conditioned for two weeks in the laboratory.

Colour measurements

Changes in colour are among the first and simplest indicators of changes in the wood. Two radial sides of each sample (five in total per treatment/aging procedure) were scanned before and after aging, and the colour in the images was evaluated with the CIE (Commission Internationale de 1'Eclairage) L*a*b* system, where L^* represents the lightness, varied from 100 (white) to 0 (black); a^* (along the X axis) red (+) to green (-) and b^* (along the Y axis) yellow (+) to blue (-) are the chromaticity coordinates. (ISO/DIS 7724-3 1997, Deka *et al.* 2008) with CorelDRAW 8 software (Ottawa, Canada). Scanning was performed with HP Scanjet G4050. Scanning parameters were adjusted for dark, semi-dark and light specimens, separately in order to obtain the most representative colour of the surface. The values reported represents the average value of two planes of the same specimen. Average colour of respective plane was calculated directly with software. It should be considered, that the whole sample was analysed. Differences in colour (ΔE) between the control specimens and the aging specimens were calculated using Eq. 1,

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

where ΔL^*, Δa^*, and Δb^* are changes between the initial and final values of L^*, a^*, and b^*, respectively.

Fourier transform infrared (FTIR) spectroscopy

Diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded between 4000 cm^{-1} and 450 cm^{-1} with a PerkinElmer FTIR Spectrum One spectrometer (Waltham, MA, USA) using Abrasive Pad 600 Grit-Coated, PK/100 paper (PerkinElmer). Spectra were collected at a 4-cm^{-1} resolution with 16 scans.

Determination of contact angles

The sessile drop method was applied to determine the contact angles of distilled water on the surfaces of specimens with a Theta optical tensiometer from Biolin Scientific Oy (Espoo, Finland). After calibration, the goniometer microscope was focused and adjusted on the image of a drop. The contact angles were measured by Young-Laplace contact angle analysis mode in OneAttension software version 2.4 (r4931) (Biolin Scientific). The shapes of drops were observed in an optical goniometer and recorded by a digital camera installed in the axial extension of the lens (Kumar *et al.* 2015). Droplets of 4 μL were applied at three different places 10 mm apart from each other on the radial

surface of five parallel specimens. In total 30 contact angles were determined per material/aging procedure. The image recording was set for 62 s (15 FPS), and the time when the contact angles started to be calculated (0 s) was after detachment of the dispenser tip from the drop, which happened approximately 2 s after the first contact of the drop with the substrate. The measurements were taken at a constant temperature of 23 °C.

Statistical analysis

All results were statistically analysed within the aging process using ANOVA (Newman-Keuls multiple range test, $p = 0.95$). Multiple range tests determined the significance of differences between the mean values at a 5% significance level and were carried out separately for each method in different aging tests.

RESULTS AND DISCUSSION

Mass Change

Changes in mass and colour are the first and most basic indicators of changes in wood specimens during artificial or natural aging. Table 2 gives the average mass changes after the aging tests. Most aging processes resulted in mass loss caused by degradation of the wood and/or leaching of extractives (Thaler *et al*. 2012). However, there were also some positive values. This was most evident with specimens exposed to blue stain fungi, whereby specimens were immersed in a malt agar suspension prior to and during fungal exposure according to the EN 152-1 standard (1996), and secondly, because fungi contribute to the mass of the specimens with their biomass and excreted compounds such as melamine. This data was consistent with previous reports (Highley 1999; Humar *et al*. 2008; Thaler *et al*. 2012).

The specimens were exposed to wood decay fungi for a shorter time than generally required, as the standard procedure takes 16 weeks, because the influence of early-stage decay was of primary interest. The purpose of this exposure was to determine whether incipient decay increases or decreases the wetting ability of wood. If the wetting ability is increased, incipient wood decay could result in an even higher moisture content (Schwarze *et al.* 2006), leading to rapid overall degradation. In spite of the short exposure time, there was a fairly high mass loss, especially after exposure to the brown rot fungus *G. trabeum.* The highest average mass loss was observed after beech wood was exposed for two months to *G. trabeum* (Fs; 39.58%). *G. trabeum* is the most important wood decay fungi for softwoods used in Class 2 and 3 applications in Central Europe. In some conditions, it also damages hardwoods (Schmidt 2006). However, the mass changes presented in Table 3 show that naturally durable wood materials (oak, chestnut), modified wood, and copper-treated wood were considerably less affected than susceptible wood (beech, pine sapwood, and spruce). Furthermore, there was considerably higher mass loss caused by *G. trabeum* than *S. commune*. *S. commune* is a prime colonizer of outdoor wood; however, it does not cause considerable mass loss in lab trials (Humar *et al*. 2001; Schmidt 2006).

The second highest average mass loss occurred after 18 months of outdoor weathering (OutDW-B) (Table 3). The most prominent mass changes during outdoor weathering was noted with larch (Ld, 7.28%), thermally modified and/or copper-treated spruce (PaTmCu, 5.64%; PaCu, 4.88%), and sweet chestnut (Cs, 4.27%). The loss of extractives (Ld, Cs) or extractable compounds (PaCu, PaTmCu) is probably the reason for this prominent mass change. Weathering is a fairly severe process that influences the

relevant properties of wood. Outdoor aging is a combination of various abiotic and biotic factors that synergistically degrade wood. However, 18 months of exposure was not sufficient to degrade wood, although it was long enough for the development of severe blue staining. The samples were too small, and they dried out too quickly for fungal degradation. Furthermore, both applied hydrophobic agents (waxes and oils) reduced the leaching of extractable compounds from the weathered specimens. For example, after 18 months of exposure, larch specimens (Ld) lost 7.28% of their mass, while oil-treated larch (LdOl) showed some mass gain (Table 3). Artificial accelerated weathering (AAW), as a pure abiotic aging procedure, also resulted in considerable mass loss. These results illustrate the importance of abiotic factors in wood aging during outdoor exposure.

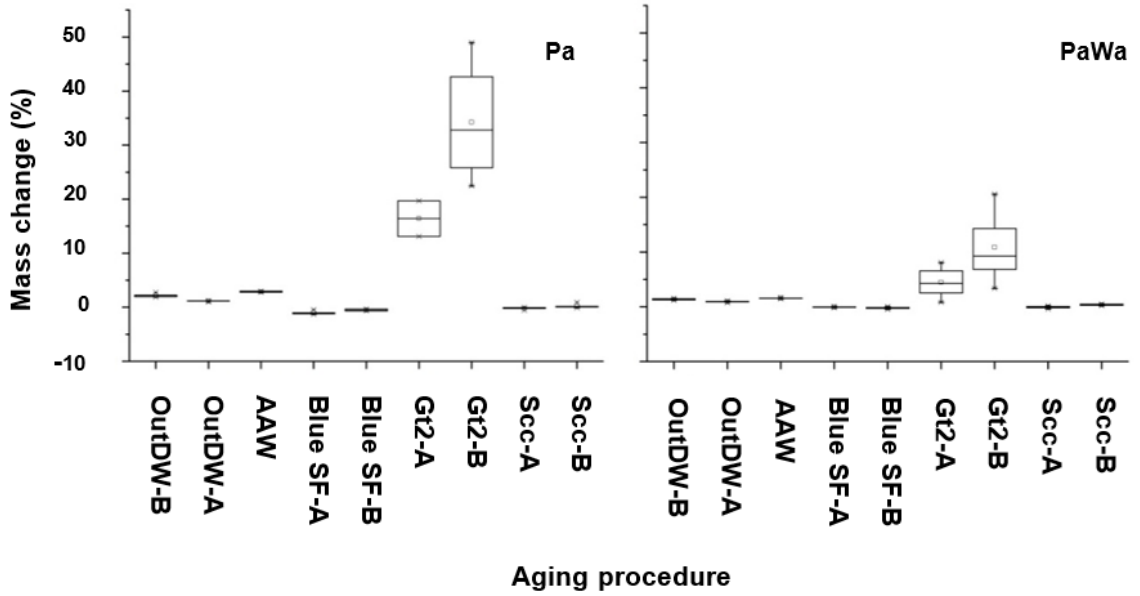

Fig. 1. Mass changes after exposure of Norway spruce (Pa) (left) and wax-treated spruce (PaWa) (right) to various aging procedures (Table 2)

Mass change during exposure to biotic factors was reduced by the application of biocides or the modification or utilisation of more durable wood, while abiotic degradation was also slightly limited by the application of hydrophobic systems (Fig. 1). To emphasise the importance of biocides, hydrophobic systems for the protection of non-durable spruce wood were also applied. Biocides in wood limit mass losses due to biotic degradation, and the hydrophobic system reduces the influence of abiotic degradation factors. Their contribution to contact angle and other surface properties are explored below.

Colour Changes

As determined by the CIELAB system, exposure to different aging factors resulted in prominent colour changes (Table 4 and 5, Fig. 2). A negative lightness difference (ΔL^*) indicated that specimens became darker, and positive numbers indicated brighter specimens. Of the colour parameters monitored, the lightness of the specimens was the most sensitive parameter. The majority of specimens became darker after exposure to different aging protocols, with the exception of specimens exposed to AAW. Most specimens that turned blue were exposed to a mixed blue stain fungi spore suspension and outdoor aging, whereby blue staining developed on the surface (Fig. 2).

Table 3. Mass Change after Different Aging Procedures Performed on Various Wooden Materials

Material	Aging Procedure																	
	AAW		Gt2-A		Gt2-B		Scc-A		Scc-B		Blue SF-A		Blue SF-B		OutDW-A		OutDW-B	
	Mass Change (% of the initial mass)																	
Cs	−3.23	F	−0.42	A	−0.44	AB	−0.43	CD	−0.34	AB	0.63	CDE	0.54	BCDE	−2.52	A	−4.27	CDE
Fs	−2.84	EF	−20.81	D	−39.58	D	−1.63	E	−7.16	C	0.16	FGH	0.09	EF	−1.59	A	−3.86	CDE
FsTm	−2.87	EF	−0.59	A	−0.66	A	−0.18	BCD	−0.39	AB	0.44	DEF	0.18	DEF	−1.80	A	−3.51	CD
FsTmWa	−1.48	C	−1.92	AB	−1.27	AB	−0.54	D	−0.72	AB	−0.23	I	−0.17	FG	−1.08	A	−1.82	ABC
Ld	−4.23	GH	−0.44	A	−1.26	AB	−0.33	CBD	−0.48	AB	0.05	GHI	0.02	EF	−5.12	A	−7.28	E
LdOl	−0.78	B	0.98	A	0.70	A	0.82	A	0.64	A	1.13	A	1.01	AB	−2.64	A	1.16	A
Pa	−2.86	EF	−16.40	CD	−34.24	CD	0.21	ABCD	−0.25	A	1.03	AB	0.52	BCDE	−1.15	A	−2.16	ABCD
PaCu	−4.05	G	−0.57	A	−0.59	A	−0.49	CD	−0.90	AB	0.89	ABC	0.75	BC	−3.74	A	−4.88	CDE
PaOl	−0.08	A	0.71	A	−7.35	AB	0.51	AB	−0.03	A	0.99	AB	1.35	A	0.85	A	−1.78	ABC
PaTm	−2.85	EF	0.09	A	−0.38	A	−0.15	BCD	−0.46	A	0.39	EF	0.18	DEF	−1.79	A	−2.29	ABCD
PaTmCu	−5.90	I	−0.30	A	−0.57	A	−0.41	CD	−0.65	AB	1.09	A	0.98	AB	−3.76	A	−5.64	DE
PaTmOl	−0.07	A	0.32	A	0	A	0.40	ABC	0.22	A	0.73	BCD	−0.53	G	0.23	A	0.23	AB
PaTmWa	−2.18	D	−0.20	A	−0.60	A	−0.50	CD	−0.69	AB	−0.71	J	−0.23	FG	−1.23	A	−1.46	ABC
PaWa	−1.57	C	−4.45	B	−10.86	B	0.10	ABCD	−0.37	AB	0.07	HIJ	0.23	CDEF	−0.92	A	−1.39	ABC
PsH	−2.60	DE	−0.14	A	−4.17	AB	−0.38	BCD	−0.80	AB	0.90	ABC	0.68	BCD	−1.43	A	−2.05	ABCD
PsS	−2.48	DE	−12.12	C	−28.48	C	−0.54	D	−4.84	BC	0.27	FG	0.05	EF	−1.78	A	−2.86	BCD
Q	−4.60	H	−0.65	A	−0.97	AB	−0.63	D	−0.95	AB	−0.12	HI	−0.05	FG	−3.17	A	−4.00	CDE

The materials and aging procedures abbreviations are the same as in Table 1 and Table 2, respectively. Statistical groups are shown in the column next to the data.

Colour changes in weathered surfaces are indicators of various biotic and abiotic factors. Chemical changes caused by UV exposure cause greying of the surface (also confirmed by FTIR analysis (Fig. 3)). In contrast, blue stain fungi darkened the wood. Comparing the AAW with naturally weathered surfaces indicated that blue staining is the prevailing factor for colour changes in this stage of outdoor exposure. AAW-aged specimens became brighter, yellowish, and reddish, while the samples weathered outdoors (OutDW-A and OutDW-B) became darker, greenish, and blueish. The main reason for this difference is that there was no development of the blue stain fungi in the control and aggressive climate during AAW, in contrast to outdoor weathering. The most prominent colour changes were determined on samples exposed to OutDW-A and OutDW-B (Fig. 2), whereby the highest ΔE (47) appears on Scots pine sapwood (PsS) and Norway spruce (Pa) specimens. On average, the least prominent colour changes were observed on samples exposed to *S. commune* (Scc-A and Scc-B), which confirms the limited degrading ability of this fungal species (Table 4) and also correlates with low mass loss (Table 3).

In terms of the susceptibility of various materials towards colour changes, the highest were determined on light-coloured, non-treated specimens. Thermally modified wood (PaTm and FsTm) exhibited much higher colour stability during different aging procedures (with the exception of AAW). The better photo-stability of thermally modified wood compared with non-modified wood could be caused by an increase in lignin stability due to condensation during thermal modification (Ayadi *et al*. 2003). Similar results were reported by Deka *et al.* (2008).

Copper-treated wood was fairly colour-stable because biocides prevent fungal discoloration, and secondly, because copper complexes in wood have a positive effect on weathering resistance. Zhang *et al*. (2009) found that copper-amine complexes stabilize the colour of treated wood and that copper-amine forms a complex with wood components and makes the wood surface more UV-resistant. Hence, better colour performance of copper-treated wood was achieved (Table 4 and 5, Fig. 2).

The colour changes of specimens treated with tung oil and an emulsion of montan wax were less prominent than those observed on untreated spruce and larch wood. For example, colour changes (expressed as ΔE) of oil-treated larch (LdOl) during AAW were 5.5 and 1.8 for wax-treated spruce (PaWa). A similar effect was observed for a transparent coating (Deka and Petrič 2008).

The low colour changes of oil- and wax-treated wood were potentially caused by better moisture performance of the wood, so that water did not leach the degraded fragments of lignin (quinone) from the wood. Additionally, the lower moisture content (MC) of hydrophobic wood reduced the radical degradation of the wood (Hon 2001) as well as fungal degradation.

A synergistic effect between thermally modified wood and waxes was also noted during colour observation. Thermally modified wood treated with waxes had the least colour change after exposure to Scc-A (ΔE 0.4). Furthermore, thermally modified wood treated with wax (PaTmWa) showed fairly low changes after being subjected to the most severe aging method (OutDW), with a ΔE of only 4.0. The positive effect of waxes on photo degradation has been reported (Lesar *et al*. 2011a), and it is mainly explained by the fact that waxes absorb part of the UV spectra and that waxes limit quinone leaching because of the reduced MC of wood.

Table 4. Colour Changes of Various Wooden Materials after Exposure to the Different Aging Tests Performed

Material	Aging Procedures																		
	Non-aged			Gt2-A				Gt2-B				Scc-A				Scc-B			
	Lp	ap	bp	Δ*L*	Δ*a*	Δ*b*	Δ*E*	Δ*L*	Δ*a*	Δ*b*	Δ*E*	Δ*L*	Δ*a*	Δ*b*	Δ*E*	Δ*L*	Δ*a*	Δ*b*	Δ*E*
Cs	72.3	4.2	10.5	-4.8	0.3	1.2	5.0	-5.4	0.0	0.9	5.5	-2.3	-0.2	0.5	2.4	-5.7	-0.4	0.3	5.7
Fs	72.1	3.9	9.1	-16.7	2.0	3.2	17.1	-12.8	1.8	4.1	13.5	-2.1	-0.2	0.1	2.2	-6.6	0.1	0.3	6.6
FsTm	27.0	3.0	4.5	4.4	1.4	2.7	5.3	-0.3	0.3	0.8	0.9	1.3	0.2	0.2	1.3	-0.1	-0.1	0.2	0.2
FsTmWa	8.9	2.2	2.1	6.1	1.8	4.0	7.5	6.4	1.1	2.8	7.1	3.2	0.4	1.3	3.5	2.3	0.2	0.8	2.5
Ld	62.4	8.3	14.4	-5.3	-0.3	1.3	5.4	-5.5	-0.3	0.7	5.5	-1.9	-0.1	1.1	2.2	-5.3	0.0	1.3	5.5
LdOl	46.2	8.4	16.1	11.8	2.9	4.8	13.1	12.7	2.2	2.5	13.1	15.7	3.3	4.4	16.6	10.6	2.5	3.1	11.3
Pa	86.2	3.2	13.5	-20.2	3.2	1.6	20.5	-22.0	3.5	2.8	22.5	-4.9	0.6	0.6	4.9	-9.3	0.7	-0.9	9.3
PaCu	56.6	1.5	10.3	-8.8	1.7	0.2	9.0	-0.9	1.0	0.9	1.6	-11.2	0.4	-1.7	11.3	-9.6	0.6	-0.6	9.6
PaOl	59.6	6.5	20.0	-10.3	2.5	1.3	10.6	-15.2	1.9	-1.5	15.3	5.8	0.7	2.5	6.3	-5.1	2.1	2.0	5.8
PaTm	29.7	3.7	5.1	1.9	1.9	3.3	4.2	2.9	1.3	2.4	4.0	2.3	0.9	1.1	2.7	0.9	0.5	0.6	1.2
PaTmCu	17.2	3.2	4.9	5.6	1.3	2.3	6.2	6.7	1.1	2.9	7.4	8.6	-0.3	-0.8	8.7	7.1	-0.1	-0.6	7.2
PaTmOl	23.7	0.6	0.2	1.9	0.8	0.8	2.2	2.7	0.8	0.7	2.9	1.8	0.6	0.4	1.9	2.0	0.8	0.7	2.2
PaTmWa	18.6	3.4	3.9	-1.5	-0.5	-0.7	1.7	0.3	-0.3	-0.1	0.5	0.3	-0.2	-0.2	0.4	1.2	-0.1	0.3	1.2
PaWa	67.4	5.5	15.0	-10.0	0.9	-0.3	10.0	-12.4	1.2	-0.1	12.5	-0.5	-0.6	-0.3	0.8	-3.3	-0.6	-1.3	3.6
PsH	77.8	5.1	12.3	-5.8	-0.3	0.3	5.9	-9.2	-0.1	-0.3	9.2	-3.7	-0.1	0.8	3.7	-7.3	-0.4	-0.4	7.3
PsS	90.2	2.3	12.2	-32.6	4.0	1.7	32.9	-37.0	4.3	1.2	37.2	-5.8	1.1	1.1	6.0	-13.9	1.6	0.5	14.0
Q	62.5	4.5	10.1	-6.6	0.1	0.5	6.6	-10.5	-0.4	0.1	10.5	-5.4	-0.1	0.2	5.4	-10.3	-0.4	-0.6	10.4

The material abbreviations are the same as in Table 1 and the aging procedures abbreviations are the same as in Table 2.

Table 5. Colour Changes of Various Wooden Materials after Exposure to the Different Aging Tests Performed

	Aging Procedures																			
	Blue SF-A				Blue SF-B				OutDW-A				OutDW-B				AAW			
Material	ΔL	Δa	Δb	ΔE	ΔL	Δa	Δb	ΔE	ΔL	Δa	Δb	ΔE	ΔL	Δa	Δb	ΔE	ΔL	Δa	Δb	ΔE
Cs	-19.8	0.0	-0.2	19.8	-20.5	-0.5	-1.1	20.5	-22.6	-2.9	-7.1	23.9	-17.8	-3.2	-7.8	19.7	16.0	-2.5	-4.8	16.8
Fs	-17.9	-0.7	-2.0	18.0	-21.4	-0.9	-2.8	21.5	-30.1	-2.8	-6.6	30.9	-25.6	-2.9	-6.9	26.7	15.1	-2.0	-3.1	15.5
FsTm	-0.1	-0.5	-1.0	1.2	2.2	0.2	0.1	2.2	12.9	-1.4	-1.4	13.1	23.1	-1.9	-2.2	23.2	43.6	-1.4	-0.3	43.6
FsTmWa	2.0	0.2	0.7	2.1	-0.1	0.2	0.3	0.4	3.8	0.1	1.6	4.1	11.9	-0.9	0.3	12.0	28.2	1.2	4.8	28.7
Ld	-17.8	-0.4	0.3	17.8	-16.1	-0.4	-0.4	16.1	-33.8	-5.7	-9.7	35.6	-31.3	-7.0	-12.2	34.3	4.3	-5.2	-9.0	11.3
LdOl	15.9	2.3	3.9	16.5	14.3	1.8	3.0	14.7	-15.1	-2.7	-8.2	17.4	-16.8	-6.1	-12.5	21.7	5.0	1.8	-1.3	5.5
Pa	-27.9	0.0	-3.9	28.1	-27.7	0.0	-4.1	27.9	-44.4	-1.8	-10.3	45.6	-45.4	-2.3	-11.6	46.9	-5.2	-0.1	-6.5	8.3
PaCu	-2.8	1.3	1.3	3.3	-1.5	1.6	1.1	2.5	-15.8	1.2	-2.9	16.2	-14.6	0.5	-5.3	15.5	0.9	2.7	0.8	2.9
PaOl	-0.8	0.6	2.1	2.3	-5.2	2.1	3.2	6.4	-37.5	-2.6	-10.2	39.0	-42.6	-4.5	-15.5	45.5	-2.8	2.6	2.3	4.5
PaTm	-2.5	-0.1	-0.5	2.5	-1.8	-0.2	-0.6	1.9	9.1	-1.1	-0.2	9.1	12.3	-2.0	-2.1	12.7	41.5	-1.4	0.5	41.5
PaTmCu	5.1	1.1	2.2	5.7	4.9	0.9	1.7	5.3	11.1	0.3	2.4	11.3	11.4	-0.7	-0.1	11.4	15.7	2.5	5.1	16.7
PaTmOl	1.4	0.4	0.4	1.5	0.8	0.1	0.0	0.8	7.1	0.9	2.6	7.6	9.1	0.0	1.7	9.3	11.3	1.1	3.4	11.8
PaTmWa	-1.2	-0.4	-0.6	1.4	-1.4	-0.5	-1.1	1.8	-3.9	0.1	1.1	4.1	-3.7	-1.2	-0.8	4.0	19.6	1.7	5.1	20.3
PaWa	-15.0	-1.1	-3.7	15.5	-14.8	-1.1	-3.7	15.3	-33.9	-3.0	-9.5	35.3	-35.6	-3.8	-11.8	37.7	0.3	1.7	-0.5	1.8
PsH	-19.2	-0.8	-2.3	19.3	-21.6	-1.1	-2.8	21.8	-29.9	-3.5	-8.9	31.3	-27.9	-4.2	-10.4	30.0	2.5	-2.6	-6.7	7.5
PsS	-35.6	-0.4	-5.6	36.0	-32.8	-0.1	-4.8	33.2	-46.2	-0.8	-8.9	47.0	-40.7	-1.5	-10.4	42.0	-7.0	1.0	-4.7	8.5
Q	-7.0	-0.3	0.4	7.0	-7.7	-0.4	-0.1	7.7	-20.2	-2.4	-4.9	20.9	-17.0	-3.4	-7.5	18.9	12.8	-1.7	-2.0	13.1

The material abbreviations are the same as in Table 1 and the aging procedures abbreviations are the same as in Table 2.

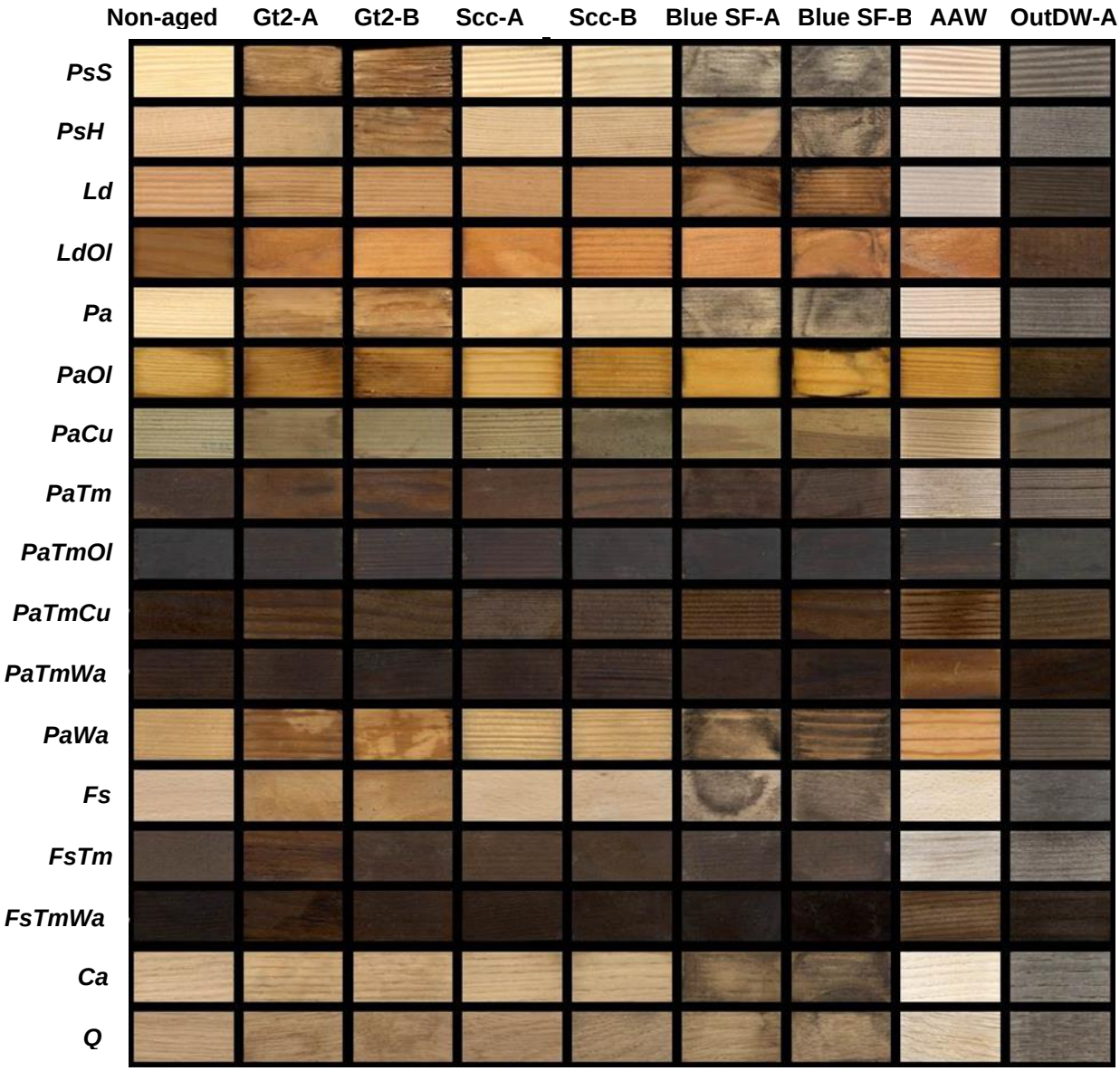

Fig. 2. Colour changes of wooden specimens after different aging tests (OutDW-B is not included because the colour changes are similar to those of OutDW-A). The materials are listed in Table 1, and the aging procedures abbreviations are listed in Table 2.

FTIR Analysis

FTIR spectra were measured for three specimens on two sides, before and after aging procedures. Only changes in non-treated spruce (Pa) and wax-treated spruce (PaWa) are reported here, as the other wood behaved very similarly. The FTIR spectra of non-aged Norway spruce (Pa) and wax-treated Norway spruce (PaWa) were not very different. The primary reason is that the amount of wax in the wood was fairly low, and wax does not have a strong characteristic band.

Next, Norway spruce was examined before and after various aging procedures. The characteristic bands of aged wood were in the region between 1600 cm^{-1} and 1050 cm^{-1}. There were no significant changes in FTIR peaks after exposure to blue stain fungi (Blue SF-A, Blue SF-B), as previously noted (Humar *et al.* 2008). Blue stain fungi do not degrade

wood, and the amount of the melanin was too low to be resolved by FTIR spectra. The weak degrader, *S. commune*, caused a few small changes in peaks assigned to lignin (1604 cm^{-1}) and xylan (1223 cm^{-1}). After eight weeks of exposure (Scc-B), this peak almost disappeared. These results are in correlation with insignificant mass changes after exposure (Table 3) and low colour changes (Fig. 2, Table 4). After exposure to the fungus *G. trabeum*, the lignin peaks changed less prominently, which was expected because this brown rot fungus decreases the content of hemicelluloses and celluloses. The band at 1050 cm^{-1}, which is assigned to the C-O valence fluctuation by cellulose and hemicellulose and the band at 1148 cm^{-1}, which is attributed to C-O-C valence fluctuation by cellulose and hemicellulose, were greatly reduced after exposure to *G. trabeum*. Changes in xylan (1221 cm^{-1}) were less visible. Changes in the absorption bands at 1604 cm^{-1}, 1658 cm^{-1}, and 1726 cm^{-1}, assigned to aromatic lignin C=C, variations in keto-carbonyl groups conjugated with the benzene ring, and C=O valence fluctuation in the xylan, respectively, were also present but less prominent.

With spruce wood exposed to AAW aging, the most prominent changes appeared at peaks 1451 cm^{-1}, 1507 cm^{-1}, and 1602 cm^{-1}. The peak at 1451 cm^{-1} denoted changes in cellulose, or more precisely, valence fluctuation in the aromatic ring in CH_2 for cellulose and aromatic lignin (1507 cm^{-1}, 1602 cm^{-1}). Chemical changes to the surface, which were confirmed on artificially weathered wood, were less prominent than with outdoor weathering. Outdoor weathering caused the most degradation of wood components. Photo-induced degradation of untreated wood led to changes in the absorption intensity at 1264 cm^{-1}, 1421 cm^{-1}, 1507 cm^{-1}, 1638 cm^{-1}, and 1731 cm^{-1}, as reported by Lesar *et al.* (2011b). These peaks showed changes in the bands related to chemical changes in the main wood components: lignin, cellulose, and hemicelluloses (Fig. 3).

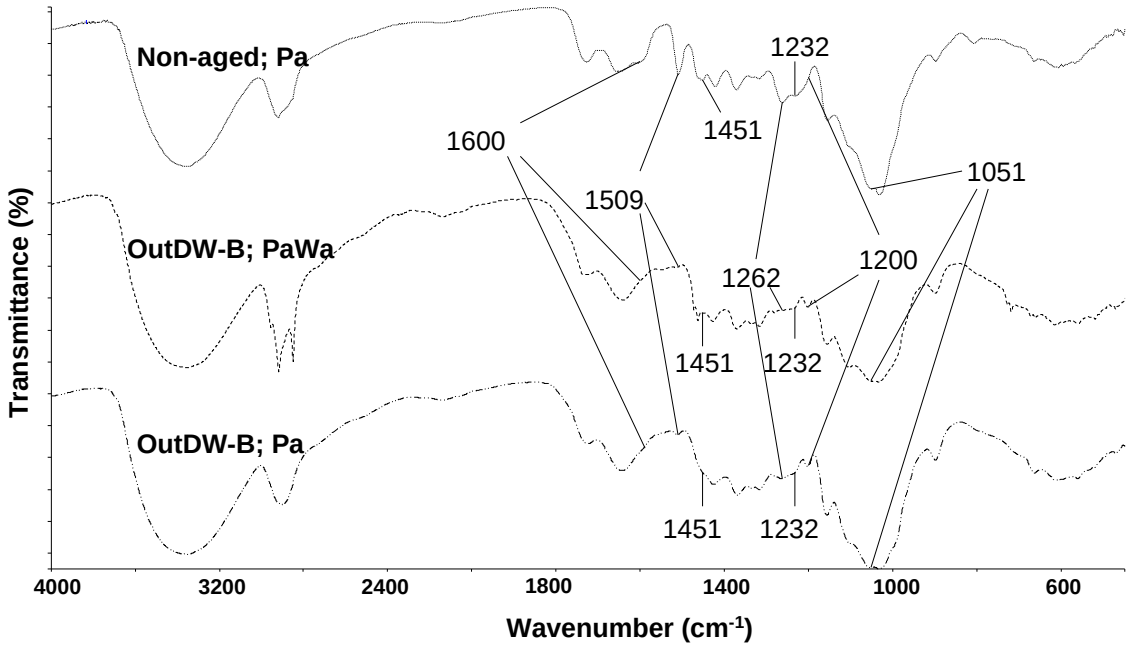

Fig. 3. FTIR spectra for non-aged Norway spruce (Pa) and for OutDW-B-aged Norway spruce (Pa) and wax-treated spruce (PaWa)

Comparison of the FTIR spectra of non-treated spruce (Pa) and wax-treated spruce (PaWa) exposed to different aging procedures revealed similar but less prominent changes. Exposure to blue stain fungus (Blue SF) and *S. commune* (Scc) did not result in changes in the FTIR spectra of wax-treated wood (PaWa), similar to spruce wood (Pa). Changes in the FTIR spectra of wax-treated spruce exposed to *G. trabeum* were similar but less prominent than those described for spruce wood. Predominantly, changes to the peak assigned to lignin (1593 cm^{-1}) were less noticeable in the presence of wax. This result confirmed that wax emulsions slow wood degradation (Lesar and Humar 2011), which is also evident from the mass losses (Table 3).

Wax treatment did not slow fungal degradation, but it did slow the photo-degradation of wax-treated wood. However, wax treatment did not block UV light completely. The most prominent changes in wood weathered outdoors (OutDW) was detected at the aromatic lignin band (1509 cm^{-1}), which almost disappeared. This result clearly indicates the initial stages of lignin UV degradation (Yildiz *et al.* 2013).

Artificially accelerated weathering (AAW) did not result in such prominent changes in the FTIR spectra as outdoor weathering (OutDW). However, some changes in peaks assigned to lignin (1600 cm^{-1}), hemicellulose (1159 cm^{-1}), and xylan (1232 cm^{-1}) cannot be overlooked; these were similar to spruce wood (Pa). Furthermore, some new peaks appeared after AAW. These peaks may appear because of surface heating during AAW, which can cause the migration of waxes to the surface. Lesar *et al.* (2011b) confirmed this hypothesis by FTIR analysis. If the present results are linked to those from that study, it can be assumed that there may be two reasons for slower photo degradation. Firstly, wax forms a layer on the surface of the wood that absorbs a certain proportion of UV irradiation (Lesar *et al.* 2011b), and secondly, the lower moisture content of wax-treated wood also contributes to slower photo degradation.

Determination of Contact Angles

Analysis of the changes in contact angle after various aging procedures was the key objective of this study. Contact angle measurement is a simple method of quantifying the surface wettability of various specimens. The limitation of this test is variability and the comparability of data from different literature sources (Petrič and Oven 2015). However, if the results are performed in the same laboratory and according to the same protocol, they can provide valuable information about hydrophobicity. These results illustrated how the wettability of hydrophobicity changes during different aging tests. The contact angles of water on the exposed surfaces of wood are important indicators of the rate of weathering (Van den Bulcke *et al.* 2011). Because water contributes to aging, various methods of hydrophobisation of wood surfaces have been investigated (Petrič and Oven 2015). Three types of hydrophobisation were used in this study: drying oil, wax emulsion, and wood modification. With some specimens, different approaches are a combined event in a single specimen, for example, wax-treated, thermally modified wood. In addition to hydrophobisation, some specimens were treated with biocides to limit biotic degradation. These materials were compared with highly durable (sweet chestnut, oak), medium-durable (larch, pine heartwood), and susceptible (pine sapwood, spruce) wood.

For each material and aging procedure, nine contact angles were determined, but only two are reported here: after the first second, when the spreading stage ended and the penetration stage began, and after one minute of contact. Fairly high contact angles after 1 s were determined on non-aged spruce (Pa, 109°), pine heartwood (PsH, 108°), pine sapwood (PsS, 94°), and larch wood (Ld, 93°) specimens.

From the measured contact angles after 60 sec, it was clear that none of these materials retained hydrophobicity after various aging procedures (Tables 5 and 6). However, naturally durable sweet chestnut (Cs, 90°) and oak (Q, 84°) were less sensitive to changes in the contact angle after outdoor weathering and exposure to wood-inhabiting fungi. This result confirmed the hypothesis that wood performance in outdoor conditions is related to the retention of hydrophobicity (Tables 5 and 6). However, larch wood and pine heartwood are less durable than oak and sweet chestnut, and neither of the former retained their hydrophobic nature after various types of aging (Tables 5 and 6). This result might explain the lower durability of these two materials, despite their fairly high extractive contents (Fengel and Wegener 1989).

Copper treatment of both spruce (PaCu) and thermally modified spruce (PaTmCu) decreased the contact angles of wood. For example, the contact angle of non-aged, untreated spruce was 109°, while considerably lower contact angles of copper-treated spruce (PaCu, 88°) were determined after 1 s (Table 5). The copper-ethanolamine wood preservative contains quaternary ammonium, a surfactant that affects wood surface properties (Thaler and Humar 2014). Furthermore, copper complexes with wood affect surface energy and, consequently, contact angles (Zhang *et al*. 2009). Copper amine treatment slows photo-degradation and fungal-infestation. Photo-degradation of lignin in particular influences contact angle and is a parameter of water exclusion efficacy. Copper treatment had a positive effect on contact angle after weathering; after fungal exposure, changes in contact angle on copper-treated wood were less prominent than on spruce wood. In certain cases, the contact angle even increased, mainly after exposure to white rot (*S. commune*). Although the starting point of non-aged spruce (Pa, 109°) was higher than that of copper-treated spruce (PaCu, 88°), the contact angle after 18 months of weathering (OutDW-B) of copper-treated spruce (PaCu, 68°) was higher than that of untreated spruce (Pa, 56°). These results are in accord with colour change and FTIR data. The colour of spruce (Pa) changed much more than copper-treated spruce (PaCu). The positive effect of copper was also evident with copper-treated, thermally modified spruce (Tables 5 and 6).

Thermal modification increased the contact angles determined on non-aged beech wood (from Fs, 76° to FsTm, 90°) and decreased the contact angles of spruce wood (from Pa, 109° to PaTm, 103°). Moderate heat treatment of beech increases its free energy, while severe thermal modification decreases free energy in spruce (Kutnar *et al.* 2013). At the beginning of thermal modification, lignin starts to degrade, but at a slower rate than polysaccharides (Windeisen *et al*. 2007; Esteves *et al*. 2008; Esteves and Pereira 2009), which contributes to a more hydrophilic surface, particularly with spruce, which was modified at higher temperatures than beech.

After aging, the contact angle of thermally modified specimens was slightly decreased (Table 5). This decrease was not particularly prominent after blue stain and wood-degrading fungi. Thermal modification makes wood more durable (Humar *et al*. 2014), and consequently, fungi did not have as great an effect as has been reported for highly susceptible spruce or beech. This effect was more evident with copper-treated, thermally modified wood, where fungal infestation was prevented to an even higher extent (Tables 5 and 6). The positive effect of thermally modified wood (PaTm, FsTm) and copper-treated, thermally modified wood (PaTmCu) on fungal disfigurement and decay also correlated with colour measurements (Table 4, Fig. 2).

Table 6. Average Influence of Various Aging Procedures on Contact Angles (°) of Water on Wood Surface Measured after 1 sec of Drop Deposition to Surface

	Aging Procedures				
Material	Non-aged	Gt2-A	Gt2-B	Scc-A	Scc-B
Cs	90 CD	89 BC	86 BCDEF	95 EFG	96 EF
Fs	76 AB	99 CDE	87 BCDEFG	85 ABCD	83 ABC
FsTm	90 CD	82 B	75 AB	84 ABC	88 BCDE
FsTmWa	114 H	105 EF	101 HI	109 HIJ	96 EF
Ld	93 CDE	89 BC	76 ABC	77 A	79 AB
LdOl	109 GH	97 CDE	87 CDEFG	93 CDEFG	81 AB
Pa	109 GH	95 CDE	97 FGH	110 IJ	98 FG
PaCu	88 CD	94 CD	93 EFGH	114 J	106 GH
PaOl	106 FGH	92 BCD	89 DEFG	99 GH	82 ABC
PaTm	103 EFG	93 BCD	81 ABCDE	94 DEFG	95 EF
PaTmCu	73 A	60 A	71 A	88 BCDEF	84 ABCD
PaTmOl	98 DEF	82 B	81 ABCD	83 AB	78 A
PaTmWa	105 FGH	88 BC	98 GH	96 FG	99 FG
PaWa	115 H	114 F	112 I	109 IJ	109 H
PsH	108 GH	102 DE	93 FGH	101 GHI	97 EF
PsS	94 CDE	95 CDE	91 DEFGH	79 AB	90 CDEF
Q	84 BC	96 CDE	94 FGH	86 ABCDE	93 DEF
Material	Blue SF-A	Blue SF-B	AAW	OutDW-A	OutDW-B
Cs	93 DEF	110 J	68 DE	82 C	90 D
Fs	74 BC	73 B	54 BC	82 C	68 BC
FsTm	71 B	75 BC	37 A	76 BC	65 ABC
FsTmWa	109 HI	106 IJ	122 I	126 E	126 E
Ld	108 GHI	112 J	36 A	63 A	60 ABC
LdOl	93 DEF	93 EFG	94 G	107 D	97 D
Pa	103 FGHI	88 DEF	77 EF	69 AB	56 AB
PaCu	84 CD	98 GHI	72 DE	67 AB	68 BC
PaOl	97 EFGH	94 EFG	86 FG	108 D	92 D
PaTm	68 B	82 CD	44 AB	70 AB	72 C
PaTmCu	54 A	56 A	50 B	67 AB	56 AB
PaTmOl	96 DEFG	77 BC	89 G	106 D	102 D
PaTmWa	96 DEFG	105 HIJ	126 I	126 E	125 E
PaWa	111 I	106 IJ	110 H	123 E	118 E
PsH	103 FGHI	112 J	55 BC	69 AB	57 AB
PsS	94 DEF	96 FGH	62 CD	66 AB	54 A
Q	87 DE	86 DE	72 DE	83 C	97 D

Abbreviations of the materials are the same as in Table 1 and aging procedures abbreviations are the same as in Table 2. Statistical groups are shown in the column next to the data.

The influence of different aging procedures and treatment methods on contact angle (CA) is shown in Tables 5 and 6. CAs measured after 1 sec were higher than those after 60 sec, which was expected (Petrič and Oven 2015). Contact angles were almost half as large after 60 sec, with the exception of material treated with wax and oil, in which there was almost no difference. For several specimens, analysis after 60 sec was not possible because the droplet had completely penetrated the specimen; these specimens were beech (Fs), thermally modified beech (FsTm), and larch (Ld) after exposure to AAW, and with spruce (Pa), pine heartwood (PsH), and pine softwood (PsS) after exposure to OutDW. These specimens had small cracks on the surface of treated and non-treated wood after exposure, which could have prevented the formation of clearly shaped droplets on the surface and may have caused the CA to decrease to 0°. Notably, zero CA appeared very quickly (a few seconds) with some samples aged in AAW and OutDW-A,B (Fs, Ld, and PsS).

The highest average CA (126°) was determined after 1 s for wax-treated, thermally modified beech (FsTmWa) and spruce (PaTmWa). Surprisingly, aged samples had higher CA values than non-aged samples. We believe that the prime reason for this occurrence originates in the fact, that during aging, emulsifiers and stabilisers that are present in wax suspension are leached out. Those additives has influence on the surface energy of the wax treated wood. The highest contact angles on wax-treated modified wood were observed with artificially accelerated weathered and outdoor-exposed specimens (126°) (Table 5). Additionally, contact angles remained constant during the 60 sec of measurement (Fig. 5), which is important from a commercial point of view because rain droplets are in contact with wood for more than one second. The good performance of weathered, wax-treated thermally modified wood was attributed to surfactants in the emulsion leaching out during weathering. Surfactants affect surface energy and are prone to leaching. The positive effect on wax-treated, thermally modified wood was due to the improved permeability and decreases hydrophobicity of modified wood, which has better penetration of waxes. Permeability of the thermally modified is increased as the piths and deposits in the cell lumina are partially degraded during thermal modification if performed at high temperatures.

There was an interesting trend in specimens treated with waxes and oil. After exposure to fungi, the contact angle slightly decreased after exposure to artificial (AAW) and outdoor weathering (OutDW) increase, as reported for weathered, wax-treated spruce (PaWa), wax-treated, thermally modified spruce (PaTmWa), and beech (FsTmWa). One of the most positive results of this study was that contact angles were improved with hydrophobic treatments such as waxes. Therefore, contact angle changes within 60 sec of contact between water and spruce and wax-treated spruce exposed to different aging tests were investigated more thoroughly (Fig. 4).

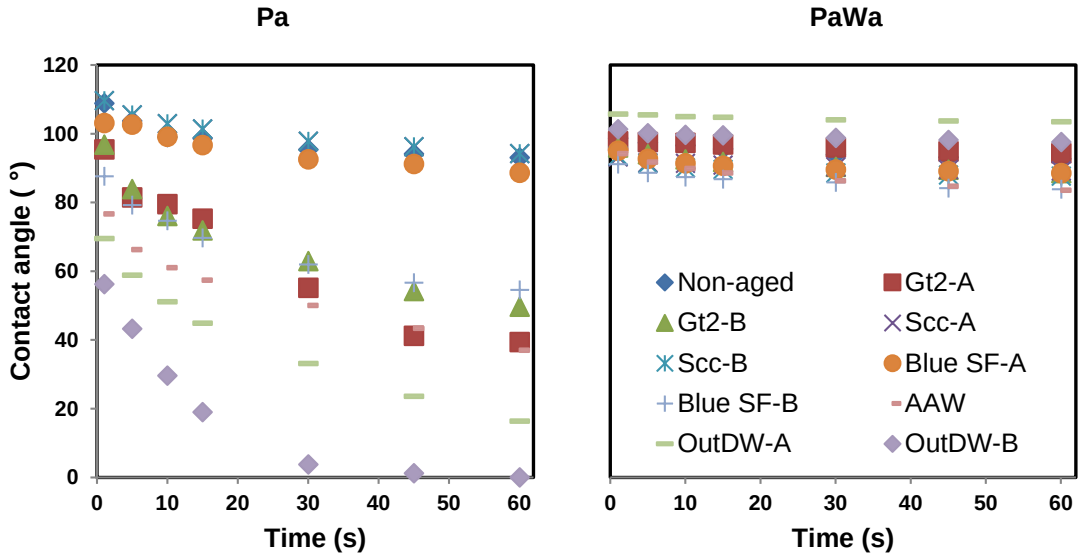

Fig. 4. Contact angles of water depending on time after drop deposition onto the surface of Pa (left graph) and PaWa (right graph), after exposure to different aging tests (Table 2). The graph shows the average numbers of all measured samples after 1, 5, 10, 15, 30, 45, and 60 sec.

Table 7. Average Influence of Various Aging Procedures on Contact Angles (°) of Water on Wood Surface Measured After 60 sec of Drop Deposition onto Surface

	Aging Procedures				
Material	Non-aged	Gt2-A	Gt2-B	Scc-A	Scc-B
Cs	55 CD	61 CDE	55 BC	64 CDE	71 CDE
Fs	40 AB	43 AB	26 A	56 ABC	54 AB
FsTm	65 DE	48 BC	50 BC	61 BCD	67 CDE
FsTmWa	110 J	89 H	88 EF	99 IJ	80 EF
Ld	71 EF	63 CDEF	49 BC	47 AB	53 AB
LdOl	101 HIJ	89 H	81 DE	87 FGHI	75 CDE
Pa	93 GH	39 AB	50 BC	94 HIJ	75 CDE
PaCu	35 A	55 BCD	50 BC	94 HIJ	74 CDE
PaOl	100 HIJ	83 GH	74 DE	91 GHIJ	77 DE
PaTm	95 HI	67 DEFG	52 BC	77 EFG	80 EF
PaTmCu	32 A	30 A	47 B	60 BC	53 A
PaTmOl	89 GH	74 EFGH	73 D	76 DEF	72 CDE
PaTmWa	99 HIJ	79 FGH	89 EF	86 FGHI	92 FG
PaWa	108 IJ	110 I	103 F	104 J	102 G
PsH	82 FG	74 EFGH	76 DE	82 FGH	74 CDE
PsS	64 DE	64 CDEF	66 CD	45 A	63 ABC
Q	49 BC	63 CDEF	52 BC	51 ABC	66 BCD
Material	Blue SF-A	Blue SF-B	AAW	OutDW-A	OutDW-B
Cs	69 CD	96 FG	37 C	54 D	44 D
Fs	45 B	32 A	0 A	12 B	1 A
FsTm	28 A	40 AB	0 A	14 B	3 AB
FsTmWa	100 FG	102 G	105 FG	123 F	123 F
Ld	91 EFG	100 G	0 A	16 B	7 ABC
LdOl	89 EFG	88 F	85 DE	95 E	76 E
Pa	89 EFG	55 CD	37 C	16 B	0 A
PaCu	54 BC	64 DE	42 C	30 C	16 BC
PaOl	86 EF	87 F	75 D	97 E	78 E
PaTm	54 BC	66 E	2 AB	5 AB	21 C
PaTmCu	20 A	32 A	12 AB	40 C	12 ABC
PaTmOl	77 DE	69 E	81 D	95 E	85 E
PaTmWa	90 EFG	101 G	112 G	126 F	122 F
PaWa	103 G	98 FG	97 EF	121 F	114 F
PsH	89 EFG	99 G	7 AB	7 AB	0 A
PsS	60 BC	70 E	15 B	0 A	0 A
Q	46 B	51 BC	31 C	40 C	41 D

Material abbreviations are the same as in Table 1 and aging procedures abbreviations are the same as in Table 2. Statistical groups are shown in the column next to the data.

Contact angles decreased during the contact with spruce wood. The lowest contact angles were found after the exposure of spruce wood (Pa) to artificial (AAW) and outdoor weathering (OutDW). Compared with spruce treated with wax (Fig. 4), it was clear that the wax-treated wood surface was more hydrophobic and that the droplet remained on the surface, even with longer periods. The highest contact angle on wax-treated wood was measured after 1 sec (123°) on a surface exposed to OutDW-A. However, even the lowest contact angle was quite high (97°) and was observed after 60 sec on wax-treated spruce wood exposed to AAW. Thus, contact angle was improved by the proper treatment. Waxes form a coating film on the surface of wood and prevent water penetration into the surface; also, there are no cracks on the surface to enable water penetration. Defined droplets were observed on the wax-treated surface of spruce wood (Fig. 5), where the highest contact angle was determined on wax-treated, thermally modified spruce and beech (PaTmWa,

FsTmWa, 126°) after 1 sec. This droplet remained stable, and contact angle changes were insignificant for a further 60 sec on wax-treated wood. However, CA significantly changed on a surface without hydrophobic treatments (Fig. 5).

Comparing the performance of wax- and oil-treated surfaces, non-aged, oil-treated spruce (PaOl) had a lower contact angle (106°) than wax-treated spruce (PaWa, 115°). Oil treatment slightly decreased the CA of spruce and thermally modified spruce and increased the CA of larch (Ld) from an initial value of 93° to 109° (LdOl) (Table 5). The exposure of oils to biotic degradation factors (fungi) decreased contact angles. For example, the contact angle of oil-treated spruce (PaOl) decreased from an initial value of 106° to a value of 89° with specimens that were exposed to *G. trabeum* for two months and 82° after the same period of exposure to *S. commune* (Table 5). With wax-treated wood, the influence of wood-degrading fungi was less significant, although no treatment had fungicidal effects.

Despite the fairly prominent mass losses (Table 5) after to the brown rot fungi *G. trabeum*, no significant decrease in CA was found. This result was evident with both less durable (spruce, pine sapwood) and more durable materials (copper-treated wood, oak, sweet chestnut). Thus, the fungus at least partly degraded or modified the surface, increasing the proportion of hydrophobic lignin, which resulted in higher contact angles after fungal degradation. The exposure of the specimens to white rot fungus was expected to have the opposite effect, but none of the materials exposed to *S. commune* had lower contact angles than the control. The highest decrease in CA was found in larch (Ld), where the CA decreased from 93° to 77° after one month of exposure to *S. commune* (Table 5). In other materials, the fungus had a positive effect on CA, *e.g.*, sweet chestnut, beech, copper-treated spruce, thermally modified spruce, and oak.

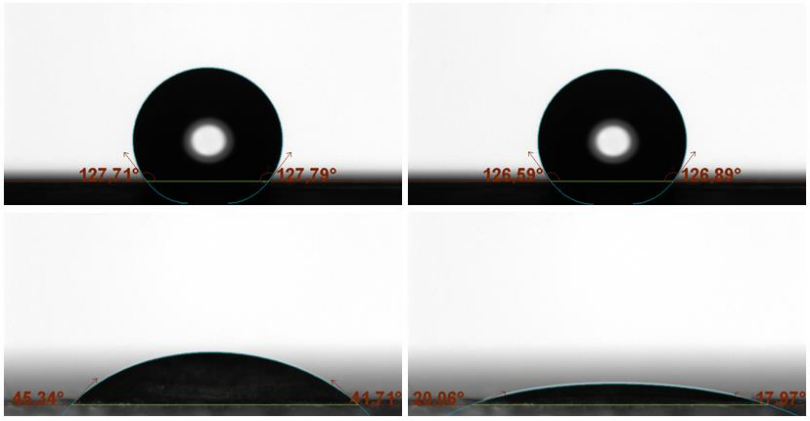

Fig. 5. Contact angles of water droplets on PaTmWa (above) after 1 sec (left) and after 60 sec (right). Below can be seen contact angles of water droplets on Pa after 1 sec (left) and after 10 sec (right) (in the next second the droplet penetrated the wood surface, so could no longer be measured).

Blue stain fungi are found even more frequently on outdoor wood than wood-degrading fungi, so their influence on surface properties has even higher commercial importance. Blue stain fungi grow on most surfaces, except those treated with biocides. However, discolorations are more visible with light-coloured wood materials. The material response to blue staining can be divided into two groups. In the first group consisting of oak, sweet chestnut, larch, pine, and copper-treated spruce, blue staining did not have an effect on the CA, or it made the surface even more hydrophobic. The opposite effect was found with beech wood, thermally modified beech, oil-treated larch, and non-modified and

modified spruce, but the reason for these changes is unclear. Most materials were at least partially blue-stained (Table 4, Fig. 2), except for larch and copper-treated wood. Fungal disfigurement on thermally modified wood was difficult to assess because of the dark colour of the wood.

CONCLUSIONS

1. Abiotic degradation (artificial accelerated weathering) had a more prominent effect on hydrophobicity than biotic factors (wood decay and blue stain fungi). Abiotic and biotic factors of degradation also acted synergistically, as shown by the comparison of contact angles on outdoor weathered and artificially accelerated weathered materials.
2. Wax- and oil-treated surfaces retained or improved hydrophobicity of the wood after various aging procedures. If waxes and oils are compared, wax-treated materials performed better after aging than oil-treated surfaces.
3. The most severe aging procedure, outdoor weathering, resulted in fairly severe chemical changes as identified by FTIR. Wax-treated surfaces were protected from photo-degradation to better extent than other materials and retained hydrophobicity after aging.
4. Durable (naturally or artificially) material retain their hydrophobic properties during the aging process. This hypothesis was tested on copper-treated spruce and thermally modified wood. Copper-treated wood was not as hydrophobic as untreated wood, but the contact angles of water on the surface after aging did not decrease as much on copper-treated wood as reported for susceptible wood materials.

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