

EFFECTS OF ARTIFICIAL WEATHERING ON THE SURFACE PROPERTIES OF COATED RADIATA PINE

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ABSTRACT

Radiata pine boards were coated with two different methods A and B both beginning with a hydro primer and finishing with a mat oil but method A using an acrylic high gloss coating and method B three layers of an acrylic sealer in between. The samples were subjected to aging processes for 144 h, 288 h, and 432 h by using UV-A 340 nm lamps. The CIE $L^*a^*b^*$ and CIE $L^*C^*H^*$ coordinates were determined (L^* , a^* , b^* , C^* , h^{o*} , ΔE^*), gloss (perpendicular (\perp) and parallel ($//$) to the grain at 20°, 60°, and 85° angles) and surface adhesion strength via the pull-off method were tested before and after weathering. Results have shown that lightness (L^*), decreases with weathering for both varnish applications with a higher decrease for the B coating system. Redness increased for both applications with no significant differences. At the same time there was a yellowing of the samples along the weathering period. Parallel and perpendicular gloss decreased for 20° and 60° angles while it increased for 85° angle. The adhesion strength of method A was higher and its decrease with weathering was smaller than for method B. Both varnish applications have proven to confer some protection against wood discoloration, but method A showed the best results and is therefore the best method to be used by radiata pine.

Keywords: Artificial weathering, color, glossiness, *Pinus radiata*, varnish applications, wood discoloration.

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INTRODUCTION

Wood weathering is a phenomenon that deteriorates wood when exposed to weather conditions. The main abiotic effects that significantly contribute to wood degradation are sunlight and rain that change the equilibrium moisture content of wood leading to cyclic wetting and drying has mentioned by Kropat *et al.* (2020). These constant variations in equilibrium moisture content change wood dimensions and lead to the formation of microcracks in wood that ultimately grow into macrocracks giving access to the sublayers under the surface (Feist 1982, Sandberg 1999). Moreover, temperature has also been reported to have a significant impact on wood degradation due to weathering (Ayata *et al.* 2017, Liu *et al.* 2017, Tolvaj *et al.* 2013). At the same time several fungi are known to alter the wood surface. The gray color of wood exposed outside has been attributed to the colonization of blue stain fungi such as *Aureobasidium pullulans* and *Sclerophoma pithyophila* (Humar *et al.* 2008, Kropat *et al.* 2020). The degree of surface changes is highly dependent on the use of wood above-ground or in-ground contact, on the natural durability of wood and also on the type of coating. The in-ground contact degradation is higher due to the constant availability of water an abundance of wooden-attacking organisms while in above-ground there are fewer organisms and more difficulty to transport moisture into fungi thallus (Goodell *et al.* 2020).

Accelerated weathering is very important in the coating industry since they can be used to simulate natural weathering spending much less time than would be needed to have results. Another reason is that accelerated weathering allows the specification of conditions such as UV radiation attributes, moisture levels or temperatures as stated by Kropat *et al.* (2020). Most researchers with wood-coating use equipment that combine some parameters such as temperature, UV irradiance, and humidity (spraying or condensation), that can be easily controlled and that accelerate the natural course of weathering (Van den Bulcke *et al.* 2008). The main difference is that artificial weathering is not subjected to biotic effects. Nevertheless, the main changes occurring on wood exposed outdoors still happen when wood is exposed to artificial weathering.

The color changes are the first to be noticed and are generally linked to natural color of wood. It is well known that initially, lighter woods become darker while darker woods become lighter (Kucuktuvek *et al.* 2017, Olărescu *et al.* 2014, Temiz *et al.* 2006). After this first stage both kinds of wood tend for a gray tone that remains stable and similar regardless of the initial wood color (Kropat *et al.* 2020, Liu *et al.* 2019). With artificial weathering this gray tone has been attributed to the washing of the degraded lignin from the surface exposing the cellulose fibers. Chemically, weathering is known to decrease the amount of lignin and somewhat hemicelluloses and to increase the cellulose content near the weathered surface (Kropat *et al.* 2020). Color changes have been associated with the degradation of extractives and lignin into quinones (Arpaci *et al.* 2021, Kishino and Nakano 2004). The changes in wood color are limited to about 2,5 mm from the surface which has been recognized as being due to the small penetration of ultraviolet and visible light into wood (Reinprecht *et al.* 2018, Sandberg 1999, Schnabel *et al.* 2009). Experiments on the photodegradation of wood found depths as far as 540 μm (Buchner 2021, Kataoka *et al.* 2007). The photodegradation depth has been proven to also depend on wood density. Kataoka *et al.* (2005) studied artificial weathering of Hinoki and Sugi and reported that the maximum depth of photodegradation increased for lower wood density which could explain why earlywood degrades faster than latewood. Once UV degradation compounds are leached from the wooden surface, the underlying layers are uncovered and similarly degraded (Buchner 2021, Reinprecht *et al.* 2018).

With artificial weathering there are also some changes on surface wettability and these changes depend on the species as seen before (Jankowska 2015, Jankowska *et al.* 2018). In accordance with Kishino and Nakano (2004) lignin degradation leads to a cellulose-rich layer that has a higher amount of hydroxyl groups and therefore of places where water can be adsorbed. Moreover, the appearance of surface cracks and rising wood fibers also contributes to the increased wettability Jankowska *et al.* (2014).

Gloss of the surface also seems to depend on the initial gloss of wood. For untreated wood gloss generally, it is known to decrease with weathering which has been attributed to physical degradation. According to Temiz *et al.* (2005) after the initial color change and loss of gloss there is an increase in surface roughness followed by checking. These authors determined the roughness increase after 200 h, 400 h and 600 h exposure to artificial weathering of Scots pine (*Pinus sylvestris*) and alder (*Alnus glutinosa*).

Varnishes are applied on wood in order to protect it from natural weathering. The main protection is due to the water repellence nature of these varnishes that, if well applied, do not allow the contact of water with wood, thus avoiding the normal shrinking and swelling happening with the rain cycles. Even when using transparent hydrophobic coatings, the service life can be prolonged by decreasing their moisture content (Pánek *et al.* 2017). Another protection attributed to varnishes is the protection from sunlight where UV light plays

a major role. Therefore, the inclusion of UV blockers on varnish formulations is common. Although high temperatures are known to influence wood weathering in accordance with Demirci *et al.* (2013) however, temperatures under 76 °C which is the maximum temperature that wood can be subjected outdoors, does not have enough thermal energy to break the chemical bonds in the adhesive. The aesthetic look of the coating is mainly influenced by color and gloss that are known to change during weathering. The changes in these parameters can be attributed to physical and chemical changes on the coating itself or in the wood underneath (Van den Bulcke *et al.* 2008). In accordance with Dickie (1994) the main effects of weathering on varnish or paint systems are cracking, loss of adhesion, and loss of gloss. Since these changes are related to physical and chemical changes this authors states that the testing of chemical and physical changes can possibly be used as a complement to accelerate aging processes. There are several articles studying the artificial weathering of radiata pine but most of them ignore the influence of different coatings that can limit the access to water and reduce the damage from UV light. This paper focuses on the artificial weathering of coated radiata pine wood with different methods in order to access the best method for radiata pine parquet.

MATERIALS AND METHODS

Materials

Wood boards of Radiata pine (*Pinus radiata* D. Don) originated from a local industry of Düzce region in Türkiye were used. The sapwood boards with dimensions 100 cm x 10 cm x 1,7 cm were purchased in a local mill.

Methods

Varnish application

Two different applications were made in accordance with the described in Table 1 in a parquet flooring company named KPS (Düzce City, Türkiye). Both applications started with a clear UV curing hydro-primer (Kneho-Lacke GmbH, Horn-Bad Meinberg, Germany) (T8028-0000) containing polyurethane acrylate and unsaturated acrylate resins dispersed in water. Then in method A, a high gloss coating (Kneho-Lacke GmbH, Horn-Bad Meinberg, Germany) (T9120-0900N1) containing glycerol and propoxylated esters with acrylic acid. In method B two different sealers, clear sealer 1 (Kneho-Lacke GmbH, Horn-Bad Meinberg, Germany) (T9110-0000H) and clear sealer 2 (Kneho-Lacke GmbH, Horn-Bad Meinberg, Germany) (T9110-0000) were used. Both methods ended with an oil clear mat for roller coating with UV curing (Kneho-Lacke GmbH, Horn-Bad Meinberg, Germany) (T9115-0000) More permonorized information about the chemicals of the different layers used in this study are presented elsewhere (Ayata 2019).

Table 1: Varnish application methods A and B.

Methodology Steps	
A	Sanding and calibrating machines (80 to 120 grit sizes)
	Clear UV curing hydro primer applied at 10 g/m ² then dried (70 °C)
	UV curtain coating high gloss applied at 8 g/m ²
	UV lamp drying (2 times) Total (177 mJ/cm ²)
	Sanding and calibrating machines (280 to 320 grit sizes)
	clear mat UV oil applied at 8 g/m ²
	UV lamp drying (71 mJ/cm ²)
	clear mat UV oil applied at 8 g/m ²
	UV lamp drying Total (2 times) (314 mJ/cm ²)
B	Sanding and Calibrating Machines (80 to 120 grit sizes)
	Clear UV curing hydro primer applied at 10 g/m ² then dried (70 °C)
	UV clear curing sealer 1 applied at 20 g/m ² then dried (70 °C)
	UV clear curing sealer 2 applied at 10 g/m ² then dried (70 °C)
	UV clear curing sealer 2 applied at 10 g/m ² then dried (170 °C)
	Sanding and Calibrating Machines (280 to 320 grit sizes)
	clear mat UV oil applied at 8 g/m ²
	UV lamp drying (71 mJ/cm ²)
	clear mat UV oil applied at 8 g/m ²
UV lamp drying Total (2 times) (314 mJ/cm ²)	

Determination of color measurement

The yellow/blue color tone (b^*), the red/green color tone (a^*), and lightness (L^*) of weathered and un-weathered coated boards were determined using a X Rite Ci62 Series Portable (X-Rite, Grand Rapids, MI, USA) (Wavelength resolution 10 nm, measurement geometry D/8°) with a D65 standard illuminant (ASTM standard D 2244-3 2007). The CIELAB system, characterized by the three axis L^* , a^* , and b^* was used. L^* represents lightness, varying from 100 (white) to zero (black), a^* is the red (+) or green (-) tone; and b^* is the yellow (+) or blue (-) tone (Esteves *et al.* 2019, Cavus 2021, Ayata *et al.* 2021a, Ayata *et al.* 2021c, Ayata *et al.* 2018). The CIE $L^*C^*H^*$ coordinates and parameters differences ΔH^* , ΔC^* , Δb^* , ΔL^* , Δa^* and ΔE^* were calculated using Equation 1, Equation 2, Equation 3, Equation 4, Equation 5, Equation 6, Equation 7 and Equation 8:

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

$$\Delta L^* = L^*_{\text{weathered coated}} - L^*_{\text{un-weathered coated}} \quad (2)$$

$$\Delta a^* = a^*_{\text{weathered coated}} - a^*_{\text{un-weathered coated}} \quad (3)$$

$$\Delta b^* = b^*_{\text{weathered coated}} - b^*_{\text{un-weathered coated}} \quad (4)$$

$$C^* = \left[(a^*)^2 + (b^*)^2 \right]^{1/2} \quad (5)$$

$$\Delta C^* = (C^*_{\text{weathered coated}}) - (C^*_{\text{un-weathered coated}}) \quad (6)$$

$$h^\circ = \arctan\left(\frac{b^*}{a^*}\right) \quad (7)$$

$$\Delta H^* = \left[(\Delta E^*)^2 - (\Delta L^*)^2 - (\Delta C^*)^2 \right]^{1/2} \quad (8)$$

Determination of glossiness measurement

Glossiness parallel (//) and perpendicular (\perp) to the grain at 20°, 60° and 85° angles in both weathered and un-weathered coated samples (100 mm x 100 mm x 17 mm) were recorded with a glossmeter (Poly gloss GL0030 TQC BV, Neuss, Germany) (ISO 2813 1994).

Determination of surface adhesion strength

The surface adhesion strength of all samples (100 mm x 100 mm x 17 mm) coated with the varnish by both methods were tested with a PosiTest AT-A (automatic) pull-off Adhesion Tester (Defelsko® corp., S/N AT11802, US) according to ASTM standard D 4541 (1995). Dolly cylinders (\varnothing 20 mm) were attached to coated samples surfaces at 20°C (room temperature). All coated samples were glued using 404 Fast Plastic Steel glue (404 Kimya and Sanayi Ticaret A.Ş., Cekmekoy/Istanbul, Türkiye), which is composed of 2,4,6-tris (dimethylaminomethyl) phenol and fixed with tools.

All test specimens were air-dried for 24 h, after and the glue residue was removed with a cutter. The adhe-

sion X (MPa) was calculated using Equation 9:

$$X = 4F / \pi d^2 \quad (9)$$

Where F is the rupture force (N) and d is the diameter of the used cylinder (mm).

Artificial weathering

The samples coated with both varnish systems were exposed in a QUV weathering tester (Q-Lab, Westlake, OH, US) using ASTM G 154-06 (2006) (18 min water spray with 0,75 W/m² light intensity, 8 h ultraviolet exposure, and 50°C temperature using UV-A 340 nm for 144 h, 288 h, or 432 h. According to Kropat *et al.* (2020) UV-A 340 nm light has a peak emission at a wavelength of 343 nm and can simulate daylight exposure.

Statistical analysis

The minimum and maximum values, average and standard deviations were determined. A two-way analysis of variance was made, and homogeneity groups were determined with the data obtained before and after weathering of both varnish applications for glossiness, color and adhesion strength using the SPSS program (Sun Microsystems, Inc., 4150 Network Circle, Santa Clara, CA, USA).

RESULTS AND DISCUSSION

Color changes with weathering

Table 2 shows the results of two-way analysis of variance for color parameters with varnish application and weathering fixed factors. Results show that interaction between both factors is significant for almost all the variables with the exception of *a** color tone. Consequently, once there was a high significance level for the cross-effects (varnish application x weathering level), single effects must be evaluated. Nevertheless, in relation to color parameters the obtained values for the different varnish application were not found significant, contrarily to the values obtained for weathering.

Table 2: Variance analysis results of color parameters.

Test	Source	df	Sum of Squares	Mean Square	F	Sig
<i>L*</i>	Varnish Application (A)	1	6,147	6,147	6,562	0,011*
	Weathering Period (B)	3	3742,344	1247,448	1331,784	0,000*
	Interaction (AB)	3	24,882	8,294	8,855	0,000*
<i>a*</i>	Varnish Application (A)	1	0,087	0,087	0,755	0,386**
	Weathering Period (B)	3	941,354	313,785	2723,622	0,000*
	Interaction (AB)	3	0,371	0,124	1,074	0,362**
<i>b*</i>	Varnish Application (A)	1	0,050	0,050	0,153	0,697**
	Weathering Period (B)	3	3182,372	1060,791	3259,306	0,000*
	Interaction (AB)	3	6,048	2,016	6,194	0,001*
<i>C*</i>	Varnish Application (A)	1	0,010	0,010	0,035	0,851**
	Weathering Period (B)	3	3926,876	1308,959	4599,616	0,000*
	Interaction (AB)	3	5,026	1,675	5,887	0,001*
<i>h°</i>	Varnish Application (A)	1	0,271	0,271	0,687	0,408**
	Weathering Period (B)	3	501,672	167,224	424,699	0,000*
	Interaction (AB)	3	2,738	0,913	2,318	0,078**

*: Significant, **: Insignificant

Table 3 presents the different color parameters for both varnish applications along the weathering period. Lightness (*L**), decreases with weathering and this decrease happened for both kinds of varnish applications. The decrease was however smaller for the type B coating, showing that this type of application is slightly better when wood is exposed to weathering. This is possible due to the three layers of sealer used in method B that were able to protect better the wood surface. Nevertheless, differences were very small and only observed after

144 h of weathering since lightness is still higher for the A system with 144 h of exposure. Homogeneity groups show that these differences can be considered as statistically different. The decrease in lightness corresponds to a darkening of the wood surface and this is important not only when wood is exposed outside but also when these boards are applied in flooring inside because the boards exposed to UV light would be more discolored than the most protected ones creating differences on the surface color. This decrease in L^* as been associated with the depolymerization of lignin and extractives due to UV light exposure (Pánek *et al.* 2017). Similar results were reported before for *Tectona grandis* L.F., *Stereospermum colais* and *Dicorynia guianensis* tested under artificial xenon light for 180 h (Liu *et al.* 2019). Studies made before show that the darkening of wood samples when exposed to weathering happens for lighter woods such as Radiata pine while darker woods become lighter (Karamanoglu and Akyildiz 2013, Pánek *et al.* 2017). The same has been reported before for instance for untreated and heat-treated *Pinus pinaster* and *Pinus radiata* woods (Esteves *et al.* 2020), where untreated pines that are very light become darker while treated samples that are originally dark become lighter. Results presented by Jankowska and Szczęśna (2011) showed that lightness of merbau, kempas and teak coated with several finishing systems decreased with artificial weathering and that this decreased depended on the coating and on the wood species. For instance, for merbau the highest change was observed for wood coated with a nitrocellulose lacquer while the highest lightness change for kempas wood was obtained with shellac lacquer and for teak for polyurethane lacquer coating. Similarly, Sivrikaya *et al.* (2011) showed that lightness changes with weathering depended on the coating material for both oak and chestnut. Lightness increased for Alkyd primer plus Alkyd stain, Alkyd primer plus Alkyd varnish, Alkyd primer, acrylic stain, and thermoplastic stain systems but decreased for alkyd-based stain (solid color).

The main difference between natural and artificial weathering is that outside wood becomes gray mainly due to wood-staining that are not present in artificial weathering (Pánek *et al.* 2017).

A positive value in the a^* axis represents the red color. It can be seen in Table 3 that with the increase of weathering the redness of the samples increases for both kinds of varnish applications. In the case of a^* no significant differences were found between both kinds of application which can be confirmed by the homogeneity groups that are similar for the samples weathered during the same period of time for both applications.

Similar results were presented before for uncoated wood. For example, artificial weathering of *Tabebuia imeginosa*, *Mezilaurus itauba*, *Manilkara huberi*, *Bagassa guianensis* and *Couratari* sp. submitted to cycles of 2000 hours of ultraviolet radiation and 400 hours of water leaching lead to an increase in a^* for short time exposures followed by a decrease for long time of exposure (Silva *et al.* 2007).

A clear yellowing of the samples could be observed along the weathering period with the increase in b^* color tone. This increase is, however observed only until 288 h of weathering after which it seems to decrease slightly. This is confirmed by the homogeneity groups. Similarly, to L^* and a^* , also b^* color tone seems to depend on the initial color of wood. For example, studies by Nzokou *et al.* (2011) with finish and unfinished ash (*Fraxinus americana*), red oak (*Quercus rubra*), and hard maple (*Acer nigrum*) exposed to artificial weathering showed that b^* increased initially followed by a decrease with the prolongation of the aging. Similar results were presented before for several wood species (Silva *et al.* 2007).

Both varnish applications confer however some protection against wood discoloration, since comparing the lightness decrease of both coated systems here with uncoated Radiata pine from the study Esteves *et al.* (2020) the maximum decrease of 18,7 % obtained here for the A system exposed for 432 h is obtained after only 150 h of exposure in the other study. In relation to a^* the maximum increase obtained here after 432 h of exposure is obtained in the study by Esteves *et al.* (2020) after only 75 h of exposure. The increase, followed by a decrease in b^* is also found for untreated wood, but rather than happening after 432 h of weathering for uncoated wood it happens after 150 h of exposure showing that both varnish applications gave some protection against discoloration by UV light. The application of UV absorbers has also proven to be able to reduce wood discoloration. For instance, Ozgenc *et al.* (2012) tested the discoloration with artificial weathering of European beech (*Fagus sylvatica*) and Scots pine (*Pinus sylvestris*) coated with different systems and concluded that the influence of coatings containing UV absorbers such as UV screeners micronized TiO_2 and UVA of hydroxyphenyl-s-triazine had very similar results nevertheless the UV screener TiO_2 had slightly better results. Nevertheless, the protection against discoloration is not permanent. Pánek *et al.* (2017) tested two hydrophobic coatings with UV stabilizers on oak wood exposed to artificial weathering and concluded that there was a rapid degradation of the coatings by UV radiation, water, and temperature leading to the formation of micro-cracks and therefore not preventing leaching of depolymerized lignin and extractives from wood. Another possibility is to use opaque systems. For example, tests made by Van den Bulcke *et al.* (2008) with different varnishes showed that opaque coatings presented just a slight color change, while the semitransparent varnishes had hi-

gher changes. Nevertheless, by using opaque systems we are hiding most of the wood attractiveness. Chroma (C^*) increased for both methods but similar homogeneity groups were found for 288 hours and 432 hours of artificial weathering. On the other hand, hue (h°) decreases with weathering for both methods.

Table 3: Results of color parameters.

Test	Varnish Application	Weathering Period	N	Mean	Change (%)	SS	HG	Minimum	Maximum	Coefficient of Variation
L^*	Method A	Unweathered	20	73,84	-	1,36	A*	71,03	75,88	1,84
		144 hours	20	66,82	↓9,51	0,75	B	65,73	68,01	1,12
		288 hours	20	63,50	↓14,00	1,01	E	62,01	65,21	1,59
		432 hours	20	59,99	↓18,76	0,54	G	59,13	60,83	0,90
	Method B	Unweathered	20	73,78	-	0,77	A	72,40	75,55	1,05
		144 hours	20	66,19	↓10,29	0,90	C	64,48	67,88	1,37
		288 hours	20	64,35	↓12,78	1,20	D	62,52	66,29	1,87
		432 hours	20	61,39	↓16,79	0,95	F	60,01	62,83	1,55
a^*	Method A	Unweathered	20	7,65	-	0,61	D	6,60	8,96	8,01
		144 hours	20	11,51	↑50,46	0,21	C	11,22	11,92	1,82
		288 hours	20	12,97	↑69,54	0,32	B	12,29	13,44	2,50
		432 hours	20	14,07	↑83,92	0,16	A*	13,83	14,34	1,15
	Method B	Unweathered	20	7,58	-	0,37	D	6,91	8,23	4,83
		144 hours	20	11,60	↑53,03	0,28	C	11,15	12,16	2,37
		288 hours	20	12,79	↑68,73	0,31	B	12,32	13,32	2,44
		432 hours	20	14,04	↑85,22	0,26	A	13,67	14,54	1,83
b^*	Method A	Unweathered	20	28,13	-	0,63	E	27,05	29,38	2,24
		144 hours	20	37,58	↑33,59	0,63	C	36,51	38,48	1,68
		288 hours	20	38,70	↑37,58	0,47	A	37,94	39,47	1,22
		432 hours	20	38,21	↑35,83	0,40	B	37,51	38,79	1,06
	Method B	Unweathered	20	27,88	-	0,45	E	26,68	28,81	1,60
		144 hours	20	37,17	↑33,32	0,49	D	36,48	38,26	1,32
		288 hours	20	38,93	↑39,63	0,71	A*	37,74	40,05	1,83
		432 hours	20	38,78	↑39,10	0,69	A	37,77	39,91	1,78
C^*	Method A	Unweathered	20	29,15	-	0,73	E	27,94	30,72	2,50
		144 hours	20	39,31	↑34,85	0,56	C	38,33	40,08	1,42
		288 hours	20	40,82	↑40,03	0,39	B	40,16	41,48	0,96
		432 hours	20	40,72	↑39,69	0,37	B	40,02	41,23	0,91
	Method B	Unweathered	20	28,89	-	0,48	E	27,72	29,87	1,68
		144 hours	20	38,94	↑34,79	0,41	D	38,34	39,87	1,05
		288 hours	20	40,98	↑41,85	0,61	AB	39,98	41,92	1,49
		432 hours	20	41,24	↑42,75	0,60	A*	40,38	42,25	1,47
h°	Method A	Unweathered	20	74,81	-	0,96	A*	72,95	76,37	1,29
		144 hours	20	72,97	↓2,46	0,53	B	71,97	73,74	0,73
		288 hours	20	71,47	↓4,46	0,58	C	70,74	72,46	0,82
		432 hours	20	69,78	↓6,72	0,32	D	69,34	70,33	0,45
	Method B	Unweathered	20	74,79	-	0,63	A	73,76	75,91	0,84
		144 hours	20	72,67	↓2,83	0,56	B	71,68	73,68	0,78
		288 hours	20	71,81	↓3,98	0,67	C	70,75	72,84	0,94
		432 hours	20	70,09	↓6,28	0,58	D	69,11	70,92	0,83

Table 4 shows the total color differences along the weathering. The total color ΔE^* increases along the weathering period as expected. Similar results were reported before for *Citrus limon* wood (Şahin *et al.* 2020) and for scots pine and alder by artificial weathering during 200-600 h (Temiz *et al.* 2005).

Table 4: Total color differences (ΔL^* , ΔC^* , ΔH^* , Δa^* , Δb^* , and ΔE^*).

Varnish Application	Weathering period	ΔL^*	Δa^*	Δb^*	ΔE^*	ΔH^*	ΔC^*
Method A	144 hours	-7,02	3,86	9,45	12,39	1,08	10,16
	288 hours	-10,34	5,32	10,57	15,71	2,00	11,67
	432 hours	-13,85	6,42	10,08	18,29	3,02	11,56
Method B	144 hours	-7,59	4,02	9,29	12,65	1,24	10,05
	288 hours	-9,43	5,21	11,05	15,43	1,79	12,09
	432 hours	-12,39	6,46	10,90	17,72	2,83	12,35

Gloss variation with weathering

Table 5 presents the results of two-way analysis of variance for gloss parallel and perpendicular to fibers with varnish application and weathering fixed factors. Similar to color the interaction between both factors is significant for almost all the variables with the exception of perpendicular gloss measured at 20°.

Surface glossiness is an important property mainly when wood is used indoors in flooring or different types of furniture since it influences the way light is dispersed across a room. Measurements were made parallel and perpendicularly to the grain and results show that there are significant differences between both directions. When the measurement is made parallel to the grain there is a clear decrease for 20° and 60° angles which can be confirmed by the different homogeneity groups seen in Table 6. The decrease however seems to be higher for the system B rather than for the A system. This can be due to some varnish degradation along the weathering period that makes it lose some of its initial gloss. Similar results were obtained before (Şahin *et al.* 2020). Weathering tests made by these authors with *Citrus limon* wood showed that gloss decreased along the weathering period although the highest changes have been observed in the first 144 h of weathering, after which glossiness stayed approximately the same.

Table 5: Variance analysis results of glossiness.

Test	Source	df	Sum of Squares	Mean Square	F	Sig.
//20°	Varnish Application (A)	1	0,256	0,256	84,961	0,000*
	Weathering Period (B)	3	4,353	1,451	481,610	0,000*
	Interaction (AB)	3	0,037	0,012	4,038	0,009*
//60°	Varnish Application (A)	1	6,602	6,602	139,998	0,000*
	Weathering Period (B)	3	62,551	20,850	442,167	0,000*
	Interaction (AB)	3	2,010	0,670	14,210	0,000*
//85°	Varnish Application (A)	1	142,695	142,695	450,924	0,000*
	Weathering Period (B)	3	75,822	25,274	79,867	0,000*
	Interaction (AB)	3	41,793	13,931	44,023	0,000*
⊥20°	Varnish Application (A)	1	0,298	0,298	111,266	0,000*
	Weathering Period (B)	3	2,683	0,894	334,374	0,000*
	Interaction (AB)	3	0,017	0,006	2,080	0,105**
⊥60°	Varnish Application (A)	1	3,969	3,969	135,388	0,000*
	Weathering Period (B)	3	24,918	8,306	283,331	0,000*
	Interaction (AB)	3	1,201	0,400	13,650	0,000*
⊥85°	Varnish Application (A)	1	0,039	0,039	6,564	0,011*
	Weathering Period (B)	3	0,460	0,153	25,750	0,000*
	Interaction (AB)	3	0,689	0,230	38,578	0,000*

*: Significant, **: Insignificant

Regarding the tests made at 85° angle there seems to be a slight increase in glossiness although it is not consistent in all the measurement periods. A similar behavior was observed for the measurements made perpendicularly to the grain with a decrease when the measurement was made at 20° and 60° angles and an increase at 85° angle. The main difference is that the glossiness values measured at 85° perpendicular to the grain have much lower values than those obtained in the parallel direction. The same inconsistency in the values measured at 85° angle were observed in the measurements perpendicular to the grain. It is known that at 85° there is a significant influence of the surface roughness which could explain these results (Bekhta *et al.* 2014). In accordance with Van den Bulcke *et al.* (2008) surface roughness effects gloss by scattering the light due to irregularities. Nonetheless, results obtained before for untreated Radiata pine (Esteves *et al.* 2020) presented

the same variations observed here with a decrease in glossiness at 20° and 65° angles and an increase at 85° angle. Similar results were presented before by Van den Bulcke *et al.* (2008) with wood coated with different varnishes. Gloss changes are different according to the kind of varnish applied on the wood surface since with weathering it's not only wood that is degraded but also the varnish. An effort has been made in the last few years to substitute solvent-based varnishes by water-based ones. For example, tests made by Van den Bulcke *et al.* (2008) with different varnishes showed that water-borne polyurethane resin coatings, still retained high reflection values not much different from the solvent-based alkyd varnishes. Sivrikaya *et al.* (2011) tested the glossiness of different coating systems applied on oak and chestnut and concluded that with weathering gloss generally decreased for most of the coating systems, especially for Alkyd stain, while the lowest decrease was obtained for Alkyd primer.

Table 6: Glossiness parallel and perpendicular to the grain measured at 20°, 60° and 85° angles.

Test	Varnish Application	Weathering Period	N	Mean	Change (%)	SS	HG	Minimum	Maximum	Coefficient of Variation	
//20°	Method A	Un-weathered	20	1,30	-	0,10	A*	1,20	1,50	7,69	
		144 hours	20	1,07	↓17,69	0,05	C	1,00	1,10	4,67	
		288 hours	20	0,98	↓24,62	0,04	D	0,90	1,00	4,08	
	Method B	432 hours	20	0,88	↓32,31	0,04	E	0,80	0,90	4,55	
		Un-weathered	20	1,26	-	0,06	B	1,10	1,30	4,76	
		144 hours	20	0,99	↓21,43	0,04	D	0,90	1,10	4,04	
//60°	Method A	288 hours	20	0,86	↓31,75	0,05	E	0,80	0,90	5,81	
		432 hours	20	0,80	↓36,51	0,00	F**	0,80	0,80	0,00	
		Un-weathered	20	7,39	-	0,32	A*	6,80	7,90	4,33	
		144 hours	20	6,25	↓15,43	0,26	C	5,80	6,70	4,16	
	Method B	288 hours	20	5,81	↓21,38	0,18	D	5,40	6,00	3,10	
		432 hours	20	6,17	↓16,51	0,20	C	5,90	6,50	3,24	
		Un-weathered	20	7,06	-	0,15	B	6,80	7,30	2,12	
		144 hours	20	6,12	↓13,31	0,27	C	5,70	6,60	4,41	
	//85°	Method A	288 hours	20	5,40	↓23,51	0,17	E**	5,20	5,90	3,15
			432 hours	20	5,42	↓23,23	0,13	E	5,20	5,60	2,40
			Un-weathered	20	9,81	-	1,02	F**	8,30	11,90	10,40
			144 hours	20	10,29	↑4,89	0,41	E	9,60	11,00	3,98
Method B		288 hours	20	10,46	↑6,63	0,21	E	10,20	10,90	2,01	
		432 hours	20	12,01	↑22,43	0,41	C	11,30	12,70	3,41	
		Un-weathered	20	12,57	-	0,83	B	11,50	13,80	6,60	
		144 hours	20	13,30	↑5,81	0,51	A*	12,60	14,10	3,83	
⊥20°	Method A	288 hours	20	11,07	↓11,93	0,32	D	10,70	12,00	2,89	
		432 hours	20	13,18	↑4,85	0,24	A	12,80	13,70	1,82	
		Un-weathered	20	1,23	-	0,09	A*	1,10	1,40	7,32	
		144 hours	20	1,02	↓17,07	0,04	C	1,00	1,10	3,92	
	Method B	288 hours	20	0,95	↓22,76	0,06	D	0,80	1,00	6,32	
		432 hours	20	0,87	↓29,27	0,05	E	0,80	0,90	5,75	
		Un-weathered	20	1,14	-	0,07	B	1,00	1,30	6,14	
		144 hours	20	0,90	↓21,05	0,00	E	0,90	0,90	0,00	
⊥60°	Method A	288 hours	20	0,88	↓22,81	0,04	E	0,80	0,90	4,55	
		432 hours	20	0,80	↓29,82	0,00	F**	0,80	0,80	0,00	
		Un-weathered	20	6,24	-	0,12	A*	6,00	6,50	1,92	
		144 hours	20	5,44	↓12,82	0,14	C	5,30	5,70	2,57	
	Method B	288 hours	20	5,10	↓18,27	0,17	D	4,90	5,60	3,33	
		432 hours	20	5,38	↓13,78	0,30	C	4,90	5,90	5,58	
		Un-weathered	20	5,88	-	0,12	B	5,70	6,00	2,04	
		144 hours	20	5,09	↓13,44	0,05	D	5,00	5,20	0,98	
⊥85°	Method A	288 hours	20	5,07	↓13,78	0,22	D	4,80	5,40	4,34	
		432 hours	20	4,87	↓17,18	0,12	E**	4,70	5,00	2,46	
		Un-weathered	20	2,43	-	0,13	B	2,20	2,80	5,35	
		144 hours	20	2,29	↓5,76	0,07	C	2,20	2,40	3,06	
	Method B	288 hours	20	2,44	↑0,41	0,08	B	2,40	2,60	3,28	
		432 hours	20	2,27	↓6,58	0,09	C**	2,10	2,50	3,96	
		Un-weathered	20	2,42	-	0,08	B	2,30	2,60	3,31	
		144 hours	20	2,52	↑4,13	0,06	A*	2,40	2,60	2,38	
	Method B	288 hours	20	2,31	↓4,55	0,04	C	2,20	2,40	1,73	
		432 hours	20	2,30	↓4,96	0,04	C	2,20	2,40	1,74	

N: Number of Measurements, SS: Standard Deviation, HG: Homogeneity Group, *: Highest, **: Lowest

Changes in adhesion strength with weathering

Two-way analysis of variance for adhesion strength with varnish application and weathering fixed factors is presented in Table 7. The interaction between both factors was likewise considered significant. Nevertheless, a significative value was obtained for the difference between the varnish applications and the weathering period for adhesion strength.

Table 7: Variance analysis results of adhesion strength.

Source	df	Sum of Squares	Mean Square	F	Sig.
Varnish Application (A)	1	11,183	11,183	79,286	0,000*
Weathering Period (B)	3	62,172	20,724	146,929	0,000*
Interaction (AB)	3	0,315	0,105	0,745	0,533**
Error	32	4,514	0,141		
Total	40	536,310			
Corrected Total	39	78,184			

*: Significant, **: Insignificant

Table 8 presents the adhesion strength of initial and weathered surfaces. The adhesion strength of method A application is higher than the adhesion strength of method B. Along the weathering period the adhesion strength of both varnish applications decreased from 5,83 MPa to 2,39 MPa and from 4,80 MPa to 1,55 MPa for method A and B, respectively. The maximum decrease corresponded to 59 % for method A and 68 % for method B. Therefore, the decrease was higher for method B which might be due to some degradation of the varnish due to weathering. The same was stated before by Sönmez *et al.* (2011) that stated that with time coatings are deteriorated due to physical, chemical, and mechanical stresses happening in artificial weathering and that these stresses change the adhesion of the coating layers on wood surface. Although adhesion strength was higher for the varnish application with less layers (method A) in accordance to Grüll *et al.* (2014) coatings with higher film thickness and semi-transparent coatings of darker color are more durable. A similar decrease with aging for the adhesion of UV cured varnishes applied to hackberry Ayata *et al.* (2021a) and cedar Ayata *et al.* (2021b) has been reported before.

Table 8: Surface adhesion strength.

Varnish Application	Weathering Period	N	Mean (MPa)	Change (%)	SS	HG	Minimum	Maximum	Coefficient of Variation
Method A	Un-weathered	5	5,83	-	0,33	A*	5,29	6,11	5,66
	144 hours	5	4,03	↓30,87	0,45	C	3,56	4,53	11,17
	288 hours	5	3,41	↓41,51	0,38	D	3,02	3,94	11,14
	432 hours	5	2,39	↓59,01	0,45	E	1,62	2,74	18,83
Method B	Un-weathered	5	4,89	-	0,48	B	4,50	5,70	9,82
	144 hours	5	2,73	↓44,17	0,37	E	2,32	3,19	13,55
	288 hours	5	2,26	↓53,78	0,25	E	1,88	2,48	11,06
	432 hours	5	1,55	↓68,30	0,21	F**	1,40	1,92	13,55

N: Number of Measurements, SS: Standard Deviation, HG: Homogeneity Group, *: Highest, **: Lowest

CONCLUSIONS

Artificial weathering decreased lightness (L^*) for both kinds of varnish applications although the decrease was higher for type A coating.

The samples became redder (a^* increase) and yellower (b^* increase) for both kinds of varnish application although b^* increased after 432 h of exposure. No significant differences were found between both kinds of application.

Gloss, parallel and perpendicular to the grain decreased for 20° and 60° angles and increase for 85° angle.

The adhesion strength was better for method A application for un-weathered and weathered wood.

Both varnish applications gave some protection against wood discoloration, nevertheless method B seems to better protect the wood surface discoloration which is probably to the three layers of acrylic sealers that were used for method B. The lower adhesion strength of method B does not seem to influence negatively the performance of the finishing system.

AUTHORSHIP CONTRIBUTIONS

S. S.: Conceptualization, formal analysis, writing-review and editing; B. E.: Investigation, writing-original draft preparation, writing-review and editing, funding acquisition; A. C.: Methodology, resources, writing-review and editing;

H. S.; Methodology; I. D.: Writing-review and editing, funding acquisition; J. F.: Writing-review and editing, funding acquisition; Ü. A.: Conceptualization, formal analysis, investigation, resources, writing-original draft preparation, writing-review and editing.

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