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Color Stabilization of Siberian and European Larch Wood Using UVA, HALS, and Nanoparticle Pretreatments

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Abstract: Reducing discoloration of wood due to photodegradation caused by ultraviolet (UV) and visible (VIS) radiation enhances its aesthetical value and prolongs the overall service life of protective coatings. In this study, the efficiency of pretreatments with different active ingredients to reduce degradation and stabilize the color of Siberian (*Larix sibirica* Ledeb.) and European larch (*Larix decidua* Mill) wood was investigated. UV absorbers (UVA), hindered amine light stabilizers (HALS) and zinc oxide nanoparticles were used in twenty different pretreatments. The ability to protect wood surface against radiation was evaluated via color and gloss change measurements during artificial ageing. The efficiency of tested color-stabilizing pretreatments differed for Siberian and European larch and not all of them reduced discoloration. The most effective pretreatments were based on a combination of UVA and HALS in a synergistic effect. Overall, the best efficiency from tested variants for larch wood generally was observed for combination of Eversorb 80 on benzotriazole basis + Eversorb 93 on a piperidinyl basis. The pretreatments did not significantly affect the gloss values. The results revealed convenient variants of stabilizers for Siberian and European larch wood and confirmed different compatibility between specific wood species and color stabilizers.

Keywords: artificial ageing; color stabilization; HALS; larch wood; pretreatment; UVA; zinc oxide nanoparticles

1. Introduction

Enhancing the durability and appearance of wood coatings is essential for the successful commercialization of forest products [1]. Wood as a copolymer of natural origin is degradable by combining both abiotic and biotic factors [2]. In outdoor applications, it is primarily a combination of UV and VIS radiation, rainwater, changes in humidity and temperature, air and dust particles flow as well as the action of molds, fungi, and insects respectively [1,3–5]. Wood surfaces in the early stages of the ageing process darken due to decomposition of lignin and extractives [3,6,7]. The depolymerized lignin and extractives are subsequently washed out from the surface by rainwater, which is associated with the lightening of the surfaces due to the increased proportion of residual cellulose [6,8]. Visible greying is caused by the deposition of dirt, dust particles or by molds and wood staining fungi interaction [9,10]. Due to changes in humidity and temperature, cracks are formed and the tearing of loosened wood fibers causes felting and plastic texture [3,10]. Visible color changes on the wood surface due to UV and VIS radiation occur even indoors [11]. The discoloration is slower compared to the changes outdoors but is also recognizable by the naked eye [12] in a relatively short time [11,13]. Since the rainwater factor does not act simultaneously, the indoor changes end with surface darkening (rarely with lightening of very dark wood). Color changes can cause aesthetic degradation and loss of morale life of the product. The mentioned degradation process may be mitigated, but it cannot be completely avoided.

There are several methods that reduce color changes in wood by modifying the surface layers as summarized in studies of Evans and others [2] and Schaller and Rogez [14]. The most commonly-used and successful method of protecting wood surfaces against solar radiation is the use of coatings [2,15,16]. Improved and long-lasting protection is provided by pigmented coatings, but their disadvantage is the loss of the original valued wood color and texture. The ability of modern transparent finishes to protect wood from radiation is still limited [17–19]. Their higher efficiency against UV and VIS radiation associated with color changes can be provided by UV absorbers [20] and HALS stabilizers [21] or by nanoparticles of pigments [22]. Several studies were performed to find possible synergies between color stabilizers and specific wood species using many types of organic and inorganic stabilizers [23]. A relatively high photostabilizing effect was found for pretreatments based on ZnO nanoparticles [24], Tinuvin types [23], Eversorb types [25], or lignin stabilizers [14] with different active ingredients. The color stabilizers can either be used as a coating additives [21,26], or can be applied as a pretreatment layer and then recoated with a commercially available coatings [27,28] to prevent leaching out and maintain their appearance [29]. Since the overall service life and adhesion of coatings to the underlying wood relate to the wood disruption due to photodegradation, the use of wood photostabilization in the first place appears to be an effective option of protection [30]. In combination with the suitable transparent coating, this application can reduce color changes in both outdoors [2] and indoors.

Larch wood combines relatively high natural durability against bio-damage [31], density and strength and aesthetically-valued texture and color [32]. This determines the larch wood for outdoor applications—such as facades, fences, windows, terraces, rails, etc.—but also for indoor ones such as staircases, floors, or massive furniture. Recently, the popularity of Siberian larch (*Larix sibirica*) with a higher annual ring density, strength and higher natural durability [31] has increased [32]. European larch (*Larix decidua*) and, to a greater extent, Siberian larch are wood species with a high acidity and extractive content (especially resins and arabinogalactans) [31,33], which complicates the application of coating systems and maintaining their long service life. Nevertheless, due to UV and visible light radiation, larch rapidly changes the original color to darker shades [13] and turns grey in direct exposures to weathering. The phenomena of wood greying has been accepted especially in Western Europe in recent years, but in other countries, the customer often requires that the original appearance of the wood be maintained, which can be ensured by the use of transparent coatings [2,21]. Therefore, the suitable photostabilization of underlying wood would significantly contribute to improving the quality and prolonging the service life of transparent coatings.

This study presents the various possibilities of photostabilization of larch wood using UV and HALS stabilizers, ZnO nanoparticles, and their combinations. It determines the most effective variant for increasing wood color stability for Siberian and European larch individually via color, gloss, and visual evaluation during artificial ageing.

2. Materials and Methods

2.1. Wood Material

The experiment was conducted using European larch (*Larix decidua* Mill) and Siberian larch wood (*Larix sibirica* Ledeb.). Each wood species was represented by 42 samples with the dimensions 60 × 50 × 20 mm (longitudinal × radial × tangential). The samples were sanded with a grain size of 120 and conditioned in laboratory conditions (20 ± 2 °C and 65% RH) to achieve equilibrium moisture content of 12% before application of color stabilizing pretreatments and subsequently before each measurement.

2.2. Application of Color Stabilizers

As in other studies, the color stabilizing ingredients were dispersed in water in 3% weight content [11,34] by stirring for 5 minutes using digital high-speed overhead stirrer WiseStir HS-100D (Witeg Labortechnik, Wertheim, Germany). Some of the pretreatments were not able to fully disperse in water (P11–P15, P18). The prepared pretreatments were applied by brush on radial surfaces exposed to irradiation. The inorganic (P1 and P2) and organic stabilizers (P3–P19) were tested in addition to the commercial product (P20). The specifications of the used pretreatments are listed in Table 1.

Table 1. Specification of used stabilizing pretreatments.

Sign	Designation	Type of Pretreatment	Specification (Active Ingredients)	Producer	Solution	
R	-	-	-	-	-	
P1	NanoByk 3840	nanoparticles	40% dispersion of ZnO nanoparticles (40 nm)	Byk, Wesel, Germany	3%	
P2	NanoByk 3860	nanoparticles	50% dispersion of ZnO nanoparticles (60 nm)	Byk, Wesel, Germany	3%	
P3	AQ5	NOR HALS	light stabilizer, further not specified	Everlight, New Taipei City, Taiwan	3%	
P4	Eversorb 80	UVA	2-Hydroxy Phenyl Benzotriazole	Everlight, New Taipei City, Taiwan	3%	
P5	Eversorb 93	HALS	Bis(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate and Methyl (1,2,2,6,6-tetramethyl-4-piperidinyl) sebacate	Everlight, New Taipei City, Taiwan	3%	
P6	Eversorb 80 + Eversorb 93	UVA + HALS	see above	Everlight, New Taipei City, Taiwan	1.5% + 1.5%	
P7	Tinuvin 5333 DW	UVA + HALS	40% active content, further not specified	BASF, Ludwigshafen, Germany	3%	
P8	Tinuvin 9945-DW	UVA	benzotriazole class	BASF, Ludwigshafen, Germany	3%	
P9	Tinuvin 1130	UVA	hydroxyphenyl-benzotriazole class	BASF, Ludwigshafen, Germany	3%	
P10	Tinuvin 5151	UVA + HALS	2-(2-hydroxyfenyl)-benzotriazoles with HALS	BASF, Ludwigshafen, Germany	3%	
P11	Tinuvin 123	HALS	based on an amino-ether functionality	BASF, Ludwigshafen, Germany	3%	*
P12	Tinuvin 99-2	UVA	hydroxyphenyl-benzotriazole class	BASF, Ludwigshafen, Germany	3%	*
P13	Tinuvin 292	HALS	Bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate and Methyl (1,2,2,6,6-pentamethyl-4-piperidyl) sebacate	BASF, Ludwigshafen, Germany	3%	*
P14	Tinuvin 99-2 + Tinuvin 292	UVA + HALS	see above	BASF, Ludwigshafen, Germany	1.5% + 1.5%	*
P15	Tinuvin 99-2 + Tinuvin 123	UVA + HALS	see above	BASF, Ludwigshafen, Germany	1.5% + 1.5%	*
P16	Tinuvin 292 + Tinuvin 1130	UVA + HALS	see above	BASF, Ludwigshafen, Germany	1.5% + 1.5%	
P17	Lignostab 1198	lignin stabilizer + HALS	lignin photooxidation inhibitor, further not specified	BASF, Ludwigshafen, Germany	3%	
P18	Lignostab 1198 + Tinuvin 1130	lignin stabilizer + HALS + UVA	see above	BASF, Ludwigshafen, Germany	1.5% + 1.5%	*
P19	Lignostab 1198 + Tinuvin 99-2	lignin stabilizer + HALS+ UVA	see above	BASF, Ludwigshafen, Germany	1.5% + 1.5%	
P20	SunCare 900	UVA	water based solution with organic light stabilizers	Bohme, Liebefeld, Switzerland	3%	

Note: * signifies types of treatment with the worst solubility in water; R means control.

2.3. Artificial Ageing (AA)

The AA test was performed in a laboratory using weathering xenon chamber Q-SUN XE3H (Q-Lab, Cleveland, OH, USA) simulating the conditions with UV irradiance between 300–400 nm (TUV) on the basis of methods performed in the study of Kataoka and Kiguchi [35]. The parameters set for the test are given in Table 2. The samples were exposed for 320 hours to these conditions. The total amount of energy during artificial ageing was about 47,856 kJ/m^2.

Table 2. Parameters of artificial ageing (AA).

UV Irradiance	Relative Humidity	Black Panel Temperature	Air Temperature	Water Spray
41 W/m^2	30%	60 °C	45 °C	off

2.4. Color Measurements

Color parameters L*a*b* were determined according to the Commission International de l´Eclairage [36] before application of stabilizers, after application of stabilizers and after 50, 160, and 320 h of artificial ageing using the spectrophotometer 600d (Konica Minolta, Tokyo, Japan). The device was set to an observation angle of 10°, d/8 geometry and D65 light source using the SCI (specular component included) method. It records the basic color parameters: L* is the lightness from 100 (white) to 0 (black); a* is the chromaticity coordinate from −60 (green) to +60 (red); b* is the other chromaticity coordinate from −60 (blue) to +60 (yellow). The relative changes in color (ΔL*, Δa*, and Δb*) between the weathered and initial state were determined [37]. The total color difference (ΔE) was calculated according to the following Equation (1)

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

Note:

ΔE_P*—total color difference of wood after pretreatment application;
ΔE_{50}*—total color difference between the initial color of wood and color after 50 h of AA;
ΔE_{160}*—total color difference between the initial color of wood and color after 160 h of AA;
ΔE_{320}*—total color difference between the initial color of wood and color after 320 h of AA.

2.5. Gloss Measurements

Gloss measurements were performed based on EN ISO 2813 [38] using the glossmeter MG268-F2 (KSJ, Quanzhou, China). Five measurements at a 60° angle for medium matt surface per sample were performed during ageing. The glossmeter was used in the direction of wood fibers. Note: ΔG_{320}*—gloss difference between the initial gloss of wood and gloss after 320 h of AA.

2.6. Visual Evaluation

In order to evaluate the visual degradation of coatings, the samples were regularly scanned using the scanner Canon 2520 MFP with 300 DPI resolution (Canon, Tokyo, Japan) before and after AA.

2.7. Statistical Analysis

The statistical evaluation was done in Statistica 12 software (Statsoft, Palo Alto, CA, USA) and MS Excel 2013 (Microsoft, Redmond, WA, USA) using mean values, standard deviations, analysis of variance (ANOVA), and Tukey´s HSD multiple comparison test at $\alpha = 0.05$ significance level.

3. Results and Discussion

3.1. Initial Properties of Tested Samples

The initial properties of tested wood species are given in Table 3.

Table 3. Initial properties of larch wood.

Wood Species	Density at 12% Moisture Content (kg/m^3)		L*		a*		b*		G*	
European larch	632.5	(17.9)	70.0	(4.1)	10.9	(1.2)	25.9	(0.8)	4.7	(0.7)
Siberian larch	652.7	(15.2)	73.9	(1.4)	7.2	(0.5)	25.0	(2.4)	4.6	(0.3)

Note: Standard deviations in parenthesis; L*,a*,b*, color parameters; G* = gloss.

3.2. Total Color Difference during AA

In a statistical analysis of variance, the effect of the wood species, the type of color stabilizing pretreatment and their interactions on the investigated properties (total color difference ΔE*, gloss value ΔG*) were evaluated as statistically significant after the AA test (Table 4).

Table 4. Statistical evaluation of significance.

Experimental Factors	Response Variables					
	ΔE_P *	ΔE_{50} *	ΔE_{160} *	ΔE_{320} *	ΔG_P *	ΔG_{320} *
Wood species (WS)	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *
Pretreatment (P)	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *
WS × P	0.00 *	0.54	0.00 *	0.00 *	0.00 *	0.00 *

* Signifies $p < 0.05$ (statistically significant at significance level of 0.05).

Total color difference ΔE* indicates the efficiency of color stabilizing pretreatments during artificial ageing. The first graph shows total color difference after application of stabilizers ΔE_P* (Figure 1). Most of pretreatments did not distinctly change the original color of larch wood, considering the fact that ΔE* < 3 is a color difference that cannot be distinguished by a subjective observer [12]. The color of European and Siberian larch was most affected by the Tinuvin 123 (HALS) pretreatment (P11).

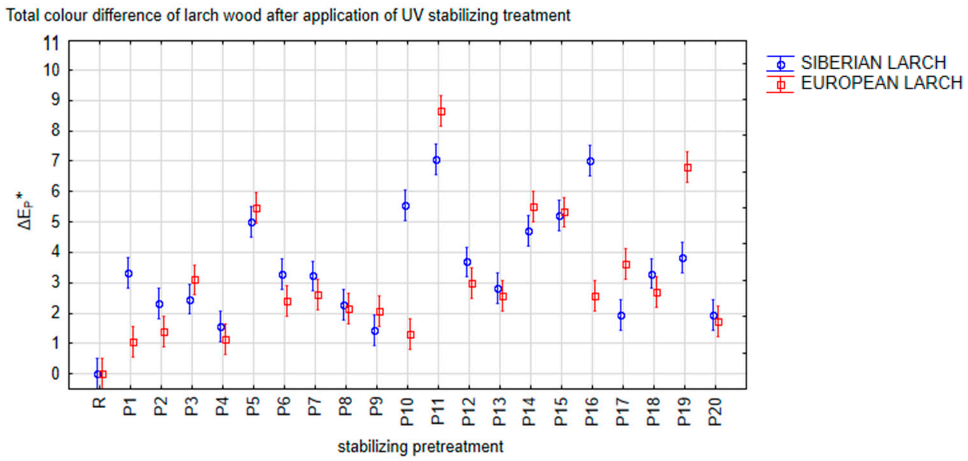

Figure 1. Total color difference of Siberian and European larch after application of stabilizing pretreatments (ANOVA results representing the 95% confidence interval in vertical bars).

The next graphs (Figure 2a–c) show total color difference of larch wood after 50, 160, and 320 h of AA compared to the color of the original untreated wood—ΔE_{50}*, ΔE_{160}*, and ΔE_{320}*. There is an increase in the total color difference of all tested samples during exposure to AA–higher changes were observed for stabilized European larch after the AA test in most cases. Some pretreatments (P3, P8, P13) were not effective at all and reached a higher color changes than the reference European larch sample. In the case of Siberian larch, all of the pretreatments reduce discoloration compared to the reference sample after AA. Nevertheless, not all of the tested variants had a statistically significant effect on the color difference reduction compared to the reference untreated larch wood (Table 5). The best performance with statistical significance for stabilizing color changes (ΔE* < 5) was observed for Tinuvin 5151 (P10) (UVA + HALS), the combination of Lignostab 1198 + Tinuvin 99-2 (P19) (lignin stabilizer + HALS + UVA) and the combination of Eversorb 80 + Eversorb 93 (P6) (UVA + HALS) for Siberian larch (Figure 2, Table 5). For European larch, the best results (ΔE* < 7) were noted for the combination of treatments Eversorb 80 + Eversorb 93 (P6) (UVA + HALS), NanoByk 3840 based on ZnO nanoparticles (P1) and Eversorb 80 (P4) (UVA)—see Figure 2, Table 5.

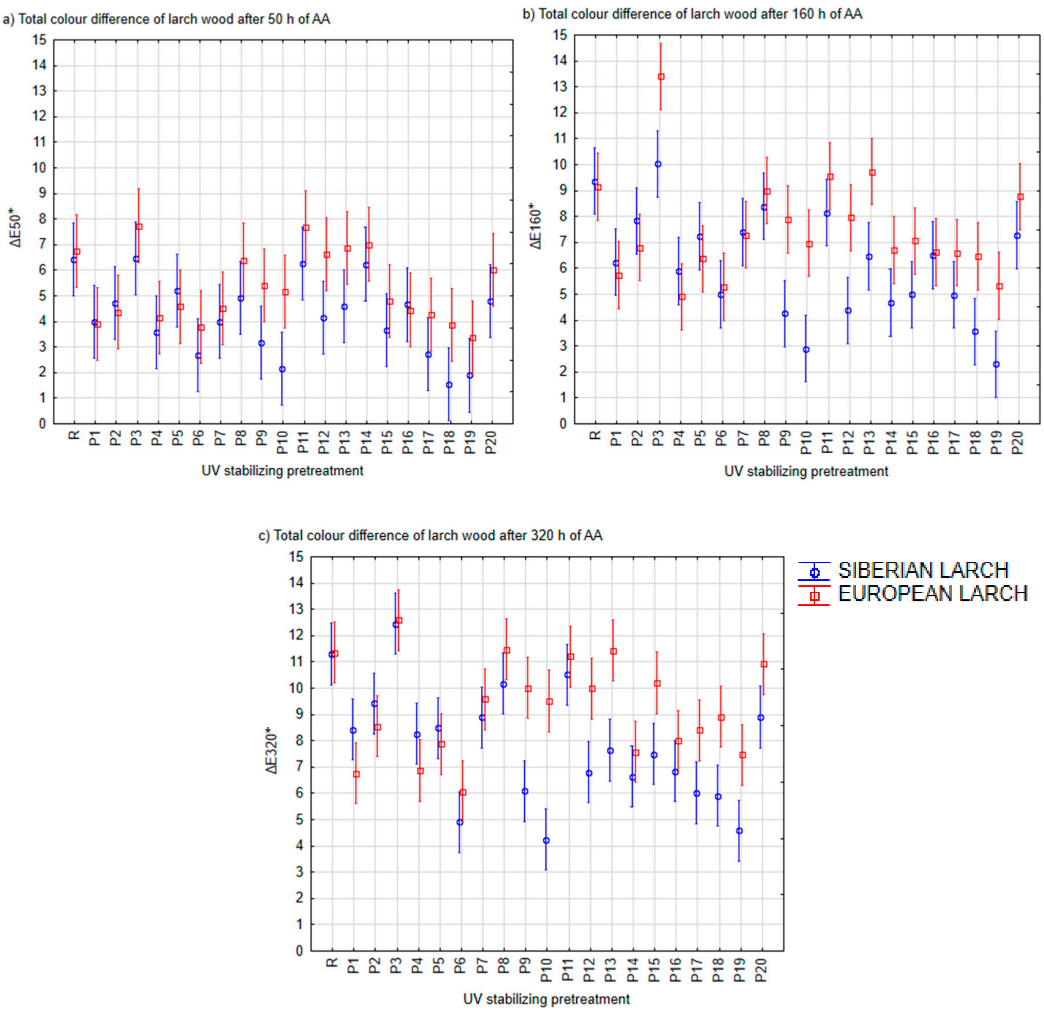

Figure 2. Total color difference of Siberian and European larch during 50 h (**a**), 160 h (**b**), and 320 h (**c**) of artificial ageing; (ANOVA results representing the 95% confidence interval in vertical bars).

3.3. Color Parameters L, a*, b* during AA*

Further investigation of color parameters L*, a*, and b* showed the differences between the durability of the tested treatments (Table 6). The statistically significant effect of pretreatment on the color parameters L*, a*, and b* was observed after AA ($p < 0.05$). The increase of values a* and b* showing a tendency for the wood surface to turn reddish and yellowish during AA and the decrease of L* (negative value) indicating a tendency to turn into darker color, was also observed in other studies [39–41]. The darkening could be directly influenced by UV absorber properties that may absorb a part of the energy created by molecular relaxation processes as noted in the work of Blanchard and Blanchett [42].

3.4. Gloss Change during AA

During AA, all of the samples were characterized by the slightly decreasing gloss value during the ageing period (Table 6). Almost all of the pretreatments had a significant effect on the gloss change reduction compared to the untreated reference (Table 5). The best performance for stabilizing gloss changes was observed for P3, P12, and P19 pretreatments for European larch. For Siberian larch, the best results were obtained with P3, P11, and P15 pretreatments (Table 5). Nevertheless, the absolute values of gloss were very low and therefore their changes ΔG* during AA are negligible in this respect.

Table 5. Effect of stabilizing pretreatment on color and gloss.

	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14	P15	P16	P17	P18	P19	P20
Effect of Pretreatment on the Total Color Difference ΔE320 *																				
European larch	0.00 * (s)	0.26	1.00	0.00 * (s)	0.02 *	0.00 * (s)	0.99	1.00	1.00	0.98	1.00	1.00	1.00	0.01 *	1.00	0.04 *	0.17	0.06	0.00 *	1.00
Siberian larch	0.21	0.97	1.00	0.12	0.25	0.00 * (s)	0.65	1.00	0.00 *	0.00 * (s)	1.00	0.00 *	0.01 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 * (s)	0.65
Effect of Pretreatment on the Total Gloss Difference ΔG320 *																				
European larch	0.00 *	0.00 *	0.21 (s)	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 * (s)	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.68 (s)	0.00 *
Siberian larch	0.00 *	0.00 *	0.00 * (s)	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.14 (s)	0.00 *	0.00 *	0.00 *	0.00 * (s)	0.00 *	0.00 *	0.00 *	0.01 *	0.00 *

* Signifies $p < 0.05$ (statistically significant at significance level of 0.05); the most stabilizing pretreatments are marked with a symbol (s).

Table 6. Change of color and gloss parameters after AA.

		R	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14	P15	P16	P17	P18	P19	P20
European Larch	ΔL_{320}*	−9.7 (1.8)	−6.1 (1.6)	−7.1 (1.1)	−8.7 (1.0)	−4.8 (3.2)	−5.9 (1.2)	−4.0 (1.2)	−7.3 (2.8)	−7.6 (2.1)	−7.9 (1.5)	−7.4 (1.7)	−9.0 (1.2)	−7.6 (2.5)	−9.6 (2.4)	−5.9 (4.4)	−7.2 (2.6)	−5.8 (2.3)	−4.9 (1.4)	−5.1 (3.0)	−4.4 (2.8)	−8.7 (1.9)
	Δa_{320}*	2.4 (0.7)	2.0 (1.4)	2.6 (0.8)	3.0 (0.6)	0.6 (1.0)	2.0 (0.7)	0.6 (0.6)	1.8 (0.7)	2.3 (1.3)	1.8 (0.7)	2.4 (1.0)	2.8 (2.5)	2.8 (1.2)	2.7 (0.8)	1.0 (2.2)	2.8 (0.8)	1.5 (1.4)	0.9 (1.8)	2.3 (1.0)	1.2 (2.5)	2.4 (0.7)
	Δb_{320}*	5.3 (1.0)	1.7 (0.9)	3.6 (1.4)	8.5 (1.7)	3.8 (1.9)	4.7 (1.1)	4.1 (1.7)	5.7 (0.8)	8.0 (0.7)	5.7 (1.2)	5.0 (2.3)	4.9 (3.9)	5.4 (2.3)	5.5 (0.7)	2.2 (1.7)	6.2 (1.2)	5.1 (1.8)	6.4 (1.0)	6.1 (1.6)	4.7 (1.2)	6.1 (0.8)
	ΔE_{320}*	11.4 (2.1)	6.8 (2.0)	8.5 (1.2)	12.6 (1.7)	6.9 (2.4)	7.9 (1.0)	6.1 (1.0)	9.6 (2.4)	11.5 (1.8)	10.0 (1.3)	9.5 (2.0)	11.2 (3.0)	10.0 (3.0)	11.4 (2.1)	7.6 (3.2)	10.2 (1.8)	8.0 (3.0)	8.4 (1.0)	8.9 (1.2)	7.5 (1.6)	10.9 (2.0)
	ΔG_{320}*	0.0 (0.5)	−2.2 (0.5)	−1.5 (0.7)	−0.8 (0.3)	−1.5 (0.5)	−1.6 (0.4)	−2.7 (0.5)	−2.9 (0.5)	−1.2 (0.2)	−2.0 (0.3)	−2.9 (1.3)	−1.3 (0.4)	−1.1 (0.4)	−1.4 (0.5)	−1.6 (0.3)	−1.7 (0.2)	−2.7 (1.1)	−1.2 (0.2)	−1.5 (0.8)	−0.6 (0.2)	−1.4 (0.3)
Siberian Larch	ΔL_{320}*	−7.7 (1.6)	−6.3 (1.1)	−7.4 (1.7)	−9.9 (0.7)	−5.9 (1.1)	−6.3 (1.6)	−2.3 (1.9)	−5.0 (1.0)	−6.5 (1.7)	−3.2 (3.4)	−0.9 (1.7)	−7.4 (1.2)	−5.4 (2.2)	−4.3 (1.9)	−3.1 (3.8)	−4.7 (1.7)	−4.5 (2.0)	−2.6 (2.2)	−2.0 (1.2)	−1.9 (0.7)	−5.9 (1.9)
	Δa_{320}*	3.0 (0.6)	3.9 (0.4)	3.6 (0.4)	4.4 (0.3)	2.5 (0.5)	2.9 (0.8)	1.6 (1.2)	2.5 (0.3)	3.3 (0.6)	1.6 (1.0)	0.4 (0.4)	3.4 (0.9)	2.2 (1.6)	1.7 (1.5)	1.6 (1.3)	1.6 (0.9)	2.6 (1.4)	1.8 (1.2)	1.9 (0.8)	0.4 (0.7)	2.2 (2.1)
	Δb_{320}*	7.4 (1.9)	3.4 (2.1)	3.9 (1.9)	6.1 (0.6)	5.2 (0.5)	4.5 (1.3)	3.6 (1.3)	6.9 (0.9)	6.8 (1.0)	4.0 (0.6)	3.8 (0.7)	6.5 (1.4)	3.2 (2.2)	5.6 (1.1)	4.5 (0.3)	5.2 (1.7)	4.0 (1.9)	4.9 (1.6)	5.0 (1.1)	4.0 (1.1)	5.9 (0.3)
	ΔE_{320}*	11.3 (1.3)	8.4 (1.1)	9.4 (1.4)	12.5 (0.8)	8.3 (1.2)	8.5 (1.2)	4.9 (1.9)	8.9 (1.2)	10.2 (0.8)	6.1 (2.4)	4.2 (1.1)	10.5 (1.4)	6.8 (3.1)	7.6 (1.0)	6.6 (2.1)	7.5 (1.4)	6.8 (2.5)	6.0 (2.5)	5.9 (1.0)	4.6 (0.8)	8.9 (1.7)
	ΔG_{320}*	−0.1 (0.3)	−2.1 (0.6)	−2.4 (0.6)	−1.2 (0.3)	−1.7 (0.2)	−2.2 (0.5)	−3.3 (0.5)	−1.6 (0.3)	−2.9 (0.3)	−2.0 (0.6)	−1.4 (0.3)	−1.0 (0.1)	−1.8 (0.6)	−1.4 (1.4)	−2.9 (0.5)	−1.2 (0.3)	−2.1 (0.5)	−2.3 (0.4)	−2.4 (0.2)	−1.2 (0.3)	−2.4 (0.3)

Note: Table represents mean values and standard deviations in parenthesis; number of measurements $n = 10$.

3.5. Visual Performance during AA

The performance during AA was also evaluated visually, which confirmed the previous results: gradual darkening and increasing the yellowness and redness of both European (Figure 3, Table 6) and Siberian larch wood (Figure 4, Table 6) during exposure. European larch is characterized by slightly higher discoloration than Siberian after AA.

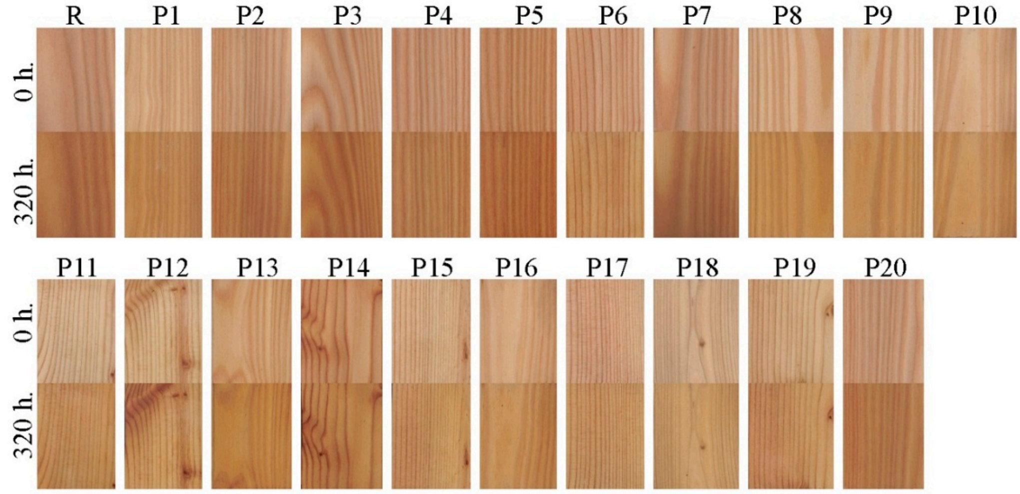

Figure 3. European larch wood with color stabilizing pretreatments (P1–P20) before and after 320 h of AA.

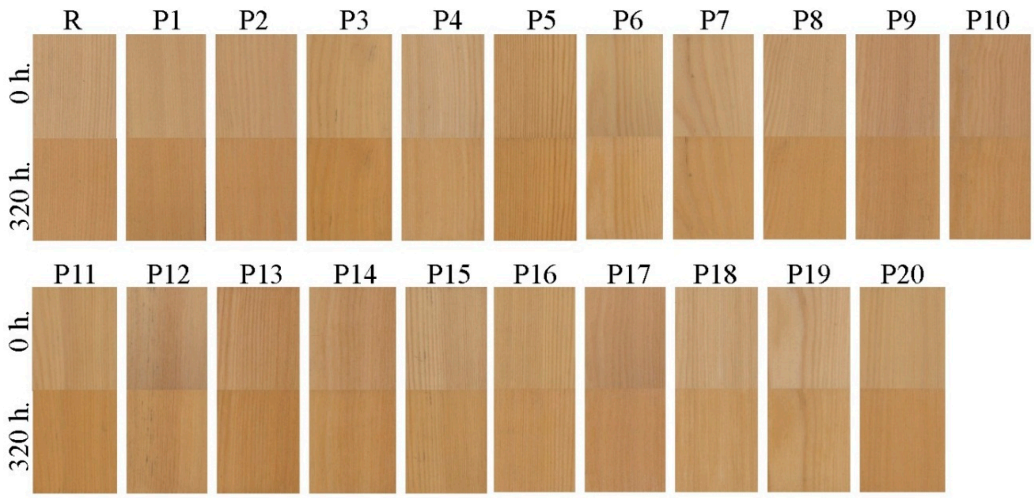

Figure 4. Siberian larch wood with color stabilizing pretreatments (P1–P20) before and after 320 h of AA.

3.6. Discussion

Discoloration due to solar radiation generally reflects chemical changes in wood during photodegradation. It can be reduced by color stabilizers, whose efficiency depends on compatibility with the polymeric material [43]. All types of color stabilizers are consumed over time, in some cases even before the end of the service life of the protected material [43]. The chemical composition varies within the genus *Larix* [44]. Siberian and European larch wood differ in the types and amounts of extractives [45] which are affected by UV and VIS radiation to a different extent [6]. Due to this specific chemical composition, the efficiency of tested color stabilizers was different. Some of the tested pretreatments proved to be inconvenient for application on larch wood from the point of view of maintaining original color, when they reached higher color changes than reference samples and some of them did not reduce the discoloration. However, some were characterized by good ability to stabilize wood color. Overall, the best efficiency from the tested variants was observed for the combination of UVA + HALS as in other studies [34,46]. The combination of UVA and HALS is generally referred to as one of the most efficient applications of color stabilizing ingredients [34,46]. The increased protection is based on the higher absorption spectra compared to the used UVA with absorbance in the region of 325–345 nm, which does not protect against UV light with longer wavelengths and harmful visible light with wavelengths up to 500 nm [11]. Forsthuber and Grüll [26] reported that HALS are able to protect the UVA against photo-oxidation. The positive effect of the UVA + HALS combination on color stabilization is obvious in this study as well for both Siberian and European larch wood (P6, P7, P10, P14–P16, P18, P19).

The ZnO nanoparticles were also characterized by good results as in the study by Mishra et al. [28], because they have a very wide absorbance band in the UV zone [1,47]. When comparing the effect of the size of zinc oxide nanoparticles (P1 × P2), there was no statistically significant difference in the total color difference after AA ($p > 0.05$) which is contrary to the study by Blanchard and Blanchett [42], where the size of nanoparticles was an important factor affecting maximum efficiency. The better UV absorption properties of metal oxides compared to the organic stabilizers reported in several studies [22,42] was not confirmed in this experiment.

The active ingredient based on NOR HALS (P3), which is the new type of HALS stabilizer, reached higher color changes after AA than the reference larch samples. The lignin protector with HALS was applied to larch wood (P17–P19). Promising results were found in the combination with Tinuvin 99-2 (UVA) applied to Siberian larch (P19). A similar combination based on lignin protector reached the best results in the study by Weichelt et al. [22]. On the other hand, the same pretreatment did not prove to be effective when applied to thermally modified beech wood [21]. The commercial pretreatment (P20) did not have a significant effect on the color stabilization of European and Siberian larch.

The obtained exact results are often variable, but they proved that the type of used wood species itself can play a significant role in prolonging the durability of the original wood color beneath the applied coating system [48–50]. The type of coating system used—especially the film-forming component type [51,52] and the type of color stabilizing treatment [50,53,54] are among the other important factors influencing performance and material durability, as was confirmed in this study. Avoiding the photodegradation of underlying wood could prolong the overall service life of wooden product [2]. The next logical step is to test whether the tested pretreatments can prevent discoloration of specific wood without affecting coating performance. The careful selection of active additives enables the formulation of coating materials with lower sensitivity to specific surface properties of larch wood and thus higher quality [32]. In addition, the coating systems (stabilizing pretreatment + available coating) can be a significant improvement of those currently commercially available and potentially applicable for European and Siberian larch wood.

4. Conclusions

The possible reduction of larch wood discoloration, which is often used outdoors and indoors and is thus exposed to the process of photodegradation—via color stabilizing pretreatments based on UVA, HALS, nanoparticles, and their combinations—was investigated in this study. The employed test methods allowed for the selection of the most durable pretreatments. Some of the tested pretreatments proved to be inconvenient for application on larch wood in terms of maintaining original color, when they reached higher color changes after artificial ageing than the reference samples, and some of them did not significantly affect the discoloration. However, some of them were characterized by good ability to stabilize larch wood color during exposure to radiation. The best ability to stabilize discoloration was observed for the combination of UVA + HALS pretreatments. Tinuvin 5151 had the best color stabilizing effect on Siberian larch wood and the combination of Eversorb 80 based on benzotriazole + Eversorb 93 based on piperidinyl performed well on European larch. The last mention combination of Eversorb 80 + Eversorb 93 (UVA + HALS) reached a good stabilizing effect on Siberian larch as well. Generally, lower discoloration was mostly observed for pretreatments applied to Siberian larch. The effect of pretreatments on the change of gloss during artificial ageing was not significant and did not vary much among the tested variants.

The exact results can often be variable, but they show that the application of color stabilizing pretreatment can be a significant improvement of available transparent coatings. As in other studies, the stabilizing effect of the UVA + HALS combination on wood during artificial ageing was proven, but with the efficiency depending on used wood species. Only careful selection of color stabilizing treatments for application on particular wood species, supported by experiments, is a key factor in color retention.

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