Characteristics of a Protective Layer on Oil Heat-Treated Scots Pine and Fir Wood

Haci Ismail Kesik,* Osman Emre Özkan, and Mustafa Öncel

Effects of natural weathering were studied relative to the adhesion strength, surface hardness, and color change of coated heat-treated and untreated Turkish fir and Scots pine wood. For this study, water-based coatings (varnish and paint) were applied on heat-treated samples. The coated heat-treated, and untreated samples were naturally weathered for one year. The difference between several properties such as adhesion strength, hardness, and color were measured before and after weathering. The test results showed that varnished heat-treated samples had good performance as compared to those of the untreated samples.

Keywords: Coated heat-treated wood; Natural weathering; Adhesion strength

*Contact information: Department of Forest Industrial Engineering, Faculty of Forestry, Kastamonu University, Kastamonu, 37150, Turkey. *Corresponding author: hismailkesik@kastamonu.edu.tr*

INTRODUCTION

Wooden material should be protected against harsh outdoor conditions. One common protection method is to impregnate the wooden material with chemicals to improve its properties (Hill 2006). For example, chromated copper arsenate (CCA) is a classic wood preservative for many applications including utility poles, children's playgrounds, and residential and commercial applications (Gezer and Cooper 2016). However, because of human health and environmental concerns, this arsenic-containing preservative has been restricted in many countries since 2004 (Hingston *et al.* 2001; Townsend *et al.* 2004; Stirling and Temiz 2014; Gezer and Cooper 2016).

The wood protection industry focuses on products and chemicals that do not have adverse effects on environmental or human health, such as thermal modification (Temiz *et al.* 2013). Heat treatment modifies the physical and chemical properties of wood using high temperatures under an inert or restricted air environment, such as nitrogen gas or oil. Treatment in hot vegetable oils is one of the alternatives to other thermal treatment methods. Treatment methods have some disadvantages because of reducing some properties of wood (Yorur *et al.* 2013). The oil heat treatment process also has some advantages, for example the absence of oxygen during treatment, uniform and quick heat transfer to wood, and surface protection by intake oil (Rapp and Sailer 2001).

Heat treatment is an effective method to improve critical wood properties. For example, improved durability, resistance against weathering factors (UV and moisture), decreased water absorption, hygroscopicity, and dimensional changes are some of the properties that are improved through heat treatment (Jamsa *et al.* 1999; Demirci *et al.* 2013; Özkan 2013; Özkan *et al.* 2014). In addition, heat treatment methods are considered as an ecological alternative to other protection methods because chemicals are not used (Korkut and Kocaefe 2009; Gezer and Cooper 2016).

Without coating, the heat-treated wood is not resistant against weathering factors (Jamsa et *al*. 2000). Application of coating on heat-treated wood may solve this problem. Also, the good dimensional stability of heat-treated wood is an advantage for durability of coatings (Akyildiz and Ates 2008). In our previous study, it was found that paint and varnish application on heat-treated Scots pine wood did not adversely affect the adhesion properties of coating layers but adhesion, hardness and color stability of coated heat-treated wood might be an issue during weathering (Kesik *et al*. 2015). The purpose of this paper was to investigate the feasibility of coated heat-treated Turkish fir and Scots pine wood for outdoor uses such as siding, garden furniture, and decking. To accomplish this purpose, effect of natural ageing on adhesion strength, surface hardness, and color change of coated heat-treated were evaluated.

EXPERIMENTAL

Materials

Turkish fir (*Abies nordmanniana* (subsp.) *bornmulleriana* (Mattf.)) and Scots pine (*Pinus sylvestris* (L.)) wood samples were cut from clear and dried sapwood harvested from the Kastamonu region of Turkey. Five replicates were used for each treatment variation. Natural weathering test samples were cut with dimensions of 10 mm × 100 mm × 100 mm (radial × tangential × longitudinal). The test samples were stored at 20 °C and 50% relative humidity for 1 week. Synthetic linseed oil was obtained from Yeni Turan Inc. (İstanbul, Turkey). The D70 water-based varnish was supplied by Kimetsan Inc. (Ankara, Turkey). The water-based paint was from Kimetsan Inc. (Ankara, Turkey), and it contained an acrylic modified polyurethane copolymer.

Methods

Oil heat treatment

The oil heat treatment was applied in a vessel filled with linseed oil for 120 min at 150 °C. After processing, the wood samples were oven-dried at 103 ± 2 °C for two days.

Water-based varnish and paint application

ASTM D3023 (2011) specifications were followed to apply coatings. The varnish and paint were applied with a spray gun without another filling layer, as two top layers. There was a waiting period of 48 h between the layers in order to dry the varnish and paint. Moreover, the dry film thicknesses of varnish and paint layers were measured in Kimetsan labs according to the ASTM D1005–95 (2013) standards. The properties of varnish and paint are shown at Table 1.

Table 1. Properties of Varnish and Paint

Protective Layer	pH	Density (g/cm^3)	Viscosity (snDINCup/4mm)	The Amount of Varnish Applied (g/m^2)	Nozzle Gap (mm)	Working Pressure (Bar)	Dry Film Thickness (µm)
Varnish	8.5	1.03	18	70	0.7	1.5	20
Paint	8.2	1.02	18	70	0.7	1.5	20

Natural weathering

Wood samples were exposed to weathering for 12 months from September 2014 to September 2015 in the Kastamonu region of Turkey. The samples were exposed to the climate factors on racks (facing to the east and at a 45° angle).

Adhesion strength (pull-off) test

Adhesion of coating films to wood has been evaluated by different methods. Among these methods, pull-off test and cross cutting test are widely used (Bardage and Bjurman 1998; Ozdemir and Hiziroglu 2007; Budakçı and Sönmez 2010). In the cross cutting test, results are dependent on applied force, cutting angle, and cutting speed according to the person performing the test (Budakçı 2006). Due to some disadvantages of the cross cutting test, the pull-off test is preferred in this study. The adhesion strength of surface layers was determined in accordance with ASTM D4541 (2009). In the test, 20 mm diameter stainless steel test cylinders were bonded with the dual-component epoxy resin Bison (Rotterdam, Netherlands) to the surface of the test samples. Then, the samples were left to dry for 24 h. The pull-off test was carried out using a universal test machine from Shimadzu. The adhesion strength (X) was calculated using Eq. 1,

$$X\ (MPa) = 4F/\pi . d^2 \tag{1}$$

where F is the rupture force (N) and d is the diameter of the test cylinder (mm).

Pendulum hardness test (Köning method)

Being widely used in Europe and Turkey, the pendulum hardness test (Karamanoğlu 2012), is based on electronic data, and the method appears to show greater sensitivity to surfaces of protective layers compared to alternative methods. The hardness of the varnish and paint layers was determined using the Köning method in accordance with ASTM D4366-95 (2002). The measuring device and the measuring range were calibrated before the test using a calibrated glass to give 100 oscillations in 40 s. Generally, harder surfaces have more oscillations than the test samples, and there are fewer oscillations on the softer surfaces.

Color measurement

The color of the wood samples was measured in accordance with ISO 7724-2 (1984) using Konica Minolta CM-2500d series spectrophotometer (Tokyo, Japan). Color was expressed in CIELab system using L^*, a^*, and b^* color coordinates. For each sample, the color coordinates of L^*, a^*, and b^* were taken from the same location before and after weathering. These values were used to calculate the color changes (ΔE^*) according to Eq. 2,

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \tag{2}$$

where ΔL^*, Δa^*, and Δb^* are the changes in color measurements before and after weathering. Changes in L^*, a^*, and b^* contribute to the color change ΔE^*. A low value of ΔE^* corresponds to low color change or stable color.

Statistical evaluation

SPSS 19 software (IBM, New York, USA) was used for statistical analysis of the data. Homogeneous groups were located according to the Duncan test, where factor effects were significant with an $\alpha = 0.05$ error rate.

RESULTS AND DISCUSSION

Adhesion Strength

An ANOVA analysis was performed to determine the effects of different factors on adhesion strength (Table 2). The weathering and application factors were statistically significant on adhesion strength ($\alpha<0.05$), whereas wood species were not statistical significant on adhesion properties. The adhesion test samples are shown in Fig. 1. Adhesion strength values of varnished wood samples were not measured because all surface layers were degraded with weathering factors.

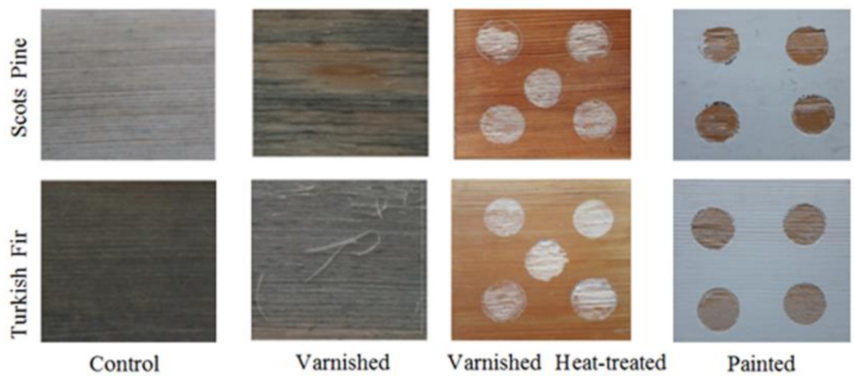

Fig. 1. Adhesion strength test samples

Natural weathering tests showed a 2% increase and 100% decrease in the adhesion strength values of varnished heat-treated and varnished pine samples, respectively. Also, natural weathering test resulted in a 28.2% and 100% reduction in the adhesion strength values of varnished heat-treated and varnished fir samples, respectively. After the natural weathering, in the painted pine samples, the decrease of adhesion strength was 18.4%, but in the case of the painted heat-treated samples the decrease of adhesion strength was 21.3%. Moreover, in the painted fir samples, reduction of adhesion strength by 23.9% was more than the painted heat-treated fir samples (12%). According to the results of the adhesion test, the coated heat-treated wood was generally found to have more resistance than the coated wood against weathering factors (Table 3). This can be explained by the contribution of surface coating and a protective lacquer coating on heat-treated materials in providing a long life protection for the wooden materials against outdoor factors (Jamsa *et al*. 2000; Çakıcıer *et al*. 2011).

Table 2. Results of Variance Analysis of Adhesion Strength Test Samples

Source of Variance*	Degrees of Freedom	Sum of Squares	Mean Square	F Value	Level of Significance
Weathering (A)	1	6,011	6.011	88.723	.00
Wood Species (B)	1	.001	.001	.008	.93
Application (C)	2	5.470	2.735	40.368	.00
A*B	1	.249	.249	3.672	.06
A*C	2	.250	.125	1.845	.16
B*C	2	1.402	.701	10.346	.00
A*B*C	2	1.349	.675	9.956	.00
Error	83	5.623	.068		
Total	95	679.983			

***:** Sources of variance are explained in Table 3.

Table 3. Comparison Results of Duncan Test for Adhesion Test Samples

Samples			Before Weathering			After Weathering			%
Wood Species	Application		$\bar{x}$*	SD	HG	$\bar{x}$	SD	HG	
Pine	Untreated	Varnish	2.85	0.26	de	-	-	-	-100
		Paint	3.09	0.18	ef	2.52	0.20	bc	-18.4
	Heat-treated	Varnish	2.06	0.12	a	2.11	0.46	a	2.4
		Paint	3.29	0.30	f	2.59	0.34	cd	-21.3
Fir	Untreated	Varnish	2.92	0.23	e	-	-	-	-100
		Paint	2.97	0.18	e	2.26	0.29	ab	-23.9
	Heat-treated	Varnish	2.84	0.17	de	2.04	0.28	a	-28.2
		Paint	2.93	0.22	e	2.58	0.37	cd	-12

$\bar{x}$: Average value, HG: Homogeneous group, SD: Standard deviation %: Percentage of difference during weathering

Surface Hardness

Weathering and application factors had a significant impact on surface hardness values, but the effect of wood species was not significant ($\alpha > 0.05$) (Table 4). The differences between the surface hardness values before and after natural weathering samples were significant.

After the natural weathering, the surface hardness test resulted in a 28.6% reduction in varnished pine samples but a 69.2% increase in varnished heat-treated pine samples. Also, the surface hardness test resulted in a 29.8% decrease in varnished fir samples, but a 50.6% increase in varnished heat-treated fir samples. After the natural weathering, the surface hardness test resulted a 66.3% increase in painted pine wood and a 55.9 increase in painted heat-treated pine. Also, the surface hardness test resulted in a 93% increase in painted fir wood and a 39.7% increase in painted heat-treated fir wood (Table 5).

According to the results of the surface hardness test, the varnished heat-treated wood was found to be more favorable than the varnished wood against weathering factors. Varnish layer hardness value is one of the most important indicators determining the durability of varnish to external factors (Atar *et al*. 2003). Therefore, heat-treatment application was required to increase the durability of varnishes against weathering factors.

Table 4. Results of Variance Analysis of the Surface Hardness Test Samples

Source of Variance	Degrees of Freedom	Sum of Squares	Mean Square	F Value	Level of Significance
Weathering (A)	1	3894.34	3894.34	162.88	.00
Wood Species (B)	1	11.90	11.90	.50	.48
Application (C)	3	6370.17	2123.39	88.81	.00
(A*B)	1	3.64	3.64	.15	.70
(A*C)	3	2767.73	922.58	38.59	.00
(B*C)	3	518.91	172.97	7.23	.00
(A*B*C)	2	261.07	130.53	5.46	.01
Error	89	2127.91	23.91		
Total	104	180227.00			

Table 5. Comparison Results of Duncan Test for Hardness Test Samples

Samples			Before Weathering			After Weathering			%
Wood	Application		x̄	SD	HG	x̄	SD	HG	
Pine	Untreated	Varnish	35.0	4.64	cd	25.0	4.53	ab	-28.6
		Paint	28.2	3.56	b	46.9	4.45	e	66.3
	Heat-treated	Varnish	38.0	7.58	d	64.3	4.82	g	69.2
		Paint	25.6	1.82	ab	39.9	3.83	d	55.9
Fir	Untreated	Varnish	28.2	3.56	b	19.8	4.53	a	-29.8
		Paint	30.0	2.55	bc	57.9	8.13	f	93
	Heat-treated	Varnish	36.4	6.11	d	54.8	4.44	f	50.6
		Paint	27.2	1.48	a	38.0	4.86	d	39.7

x̄: Average value, HG: Homogeneous group, SD: Standard deviation, %: Percentage of difference during weathering

Total Color Change (Δ*E**)

An ANOVA analysis determined the different factors effects on total color change values (Table 6). The weathering period, wood species, and application type had a significant impact on the total color change values. Exposure to sunlight and UV light caused changes on the wood surfaces. The original color of the control wood changed from brown to grey. However, the color of the varnished heat-treated wood samples was protected (Fig. 2).

Color stability values of pine samples exhibited 22.5%, 46.5%, and 58% protection in heat-treated, varnished, and varnished heat-treated samples, respectively. In fir samples, 44.1%, 33.3%, and 67% protection values in heat-treated, varnished and varnished heat-treated samples were found. According to the results of the total color change, the varnished heat-treated sample was found to be more durable than other untreated samples against weathering factors. However, there was no found positive effect of heat-treatment on color stability in paint application (Table 7). As a result, it can be said that heat-treatment is required for color stability of varnish application.

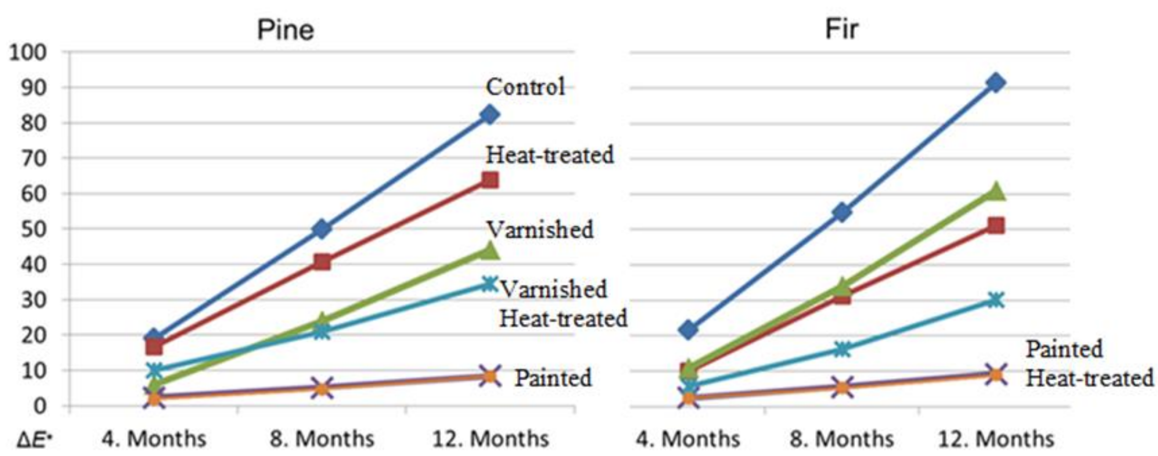

Fig. 2. Color change of wood samples

Table 6. Results of Variance Analysis of the Total Color Change Δ*E**

Source of Variance	Degrees of Freedom	Sum of Squares	Mean Square	F Value	Level of Significance
Weathering Period (A)	2	7738.61	3869.31	455.35	.00
Wood Species (B)	1	57.34	57.34	6.75	.01
Application Type (C)	5	59075.97	11815.19	1390.450	.00
(A*B)	2	110.87	55.43	6.524	.00
(A*C)	10	4444.58	444.46	52.31	.00
(B*C)	5	1880.74	376.15	44.27	.00
(A*B*C)	10	139.17	13.91	1.64	.09
Error	672	5710.25	8.50		
Total	708	205778.73			

Table 7. Comparison Results of Duncan Test for Total Color Change Δ*E**

Samples			4. Months		8. Months		12. Months		Total	%
Wood	**Application**		$\bar{x}$	**HG**	$\bar{x}$	**HG**	$\bar{x}$	**HG**		
Pine	Control		18,99	fg	30.94	l	32.25	lm	82.18	-
	Heat-treated		16.67	e	23.92	j	23.13	ij	63.72	22.5
	Untreated	Varnish	5.94	b	18.07	ef	20.02	gh	44.03	46.5
		Paint	2.37	a	2.77	a	3.33	a	8.47	89.7
	Heat-treated	Varnish	10.09	c	10.74	c	13.68	d	34.51	58
		Paint	1.86	a	2.86	a	3.61	a	8.33	89.9
Fir	Control		21.53	hi	33.38	m	36.58	n	91.49	-
	Heat-treated		10.08	c	21.16	h	19.90	fgh	51.14	44.1
	Untreated	Varnish	10.81	c	23.29	ij	26.94	k	61.04	33.3
		Paint	2.42	a	3.11	a	3.68	a	9.21	89.9
	Heat-treated	Varnish	5.77	b	10.34	c	14.07	d	30.18	67
		Paint	2.33	a	2.84	a	3.71	a	8.88	90.3

$\bar{x}$: Average value, HG: Homogeneous group, SD: Standard deviation, %: Percentage of difference during weathering

CONCLUSIONS

1. During one-year natural weathering, the performance of varnished heat-treated wood was better than that of the untreated samples. However, performance of painted heat-treated wood was not changed.
2. The weathering results indicated that oil heat-treated woods needed a protective varnish when better adhesion, hardness, and color performance were desired.
3. Thus, it is recommended that water based varnish and paint be used on the surface of oil heat-treated wood when it is to be used on exterior claddings, window joinery, and garden furniture.

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