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DETERMINATION OF PENDULUM HARDNESS (KÖNIG METHOD) VALUES AGAINST ARTIFICIAL WEATHERING IN WATER-BASED VARNISHES APPLIED TO SOME WOOD SPECIES AFTER HEAT TREATMENT (THERMOWOOD)

Scots pine, beech, and oak are the most important tree species in the furniture sector in Turkey. In this study, the aim is to determine pendulum hardness (König method) values against artificial aging in water-based varnishes applied to some wood species after heat treatment. For this purpose, Scots pine (Pinus sylvestris L.), sessile oak (Quercus petreae L.), and Eastern beech (Fagus orientalis L.) wood samples were heat-treated at 190°C for 2 h and at 212°C for 1-2 h according to the ThermoWood method. Later, one- and two-component water- -based varnishes ($WBV_{One-comp.}$ and $WBV_{Two-comp.}$) were applied to the material surfaces in accordance with the manufacturer's recommendations for layer thickness for industrial applications. The materials were exposed to UV light using UV-A 340 nm fluorescent lamps for 144, 288, and 432 h in a QUV accelerated weathering tester. After these weathering periods, pendulum hardness values were determined. It was found that hardness values increased after weathering, and that $WBV_{Two-comp.}$ gave higher values than $WBV_{One-comp.}$.

Keywords: heat treatment, pendulum hardness, artificial weathering, one- and two-component water-based varnishes

Introduction

Today, one of the environmentally friendly methods used for the protection of wood materials is heat treatment. It has been reported by various researchers that the chemical [Lukmandaru et al. 2018], surface [Kim et al. 2018], mechanical

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[Esteves et al. 2008; Won et al. 2012; Hidayat et al. 2015], physical [Bazyar 2012] and biological [Elaieb et al. 2015] properties of wood materials are altered by heat treatment. These changes have led to differences in the possible areas of outdoor use of wood. In addition, applying outdoor varnishes to heat-treated wood and investigating compatibility with outdoor conditions helps to explain the relationship between the factors of wood type, varnish type, heat treatment and weathering. This information is important for the furniture, varnish, and wood industries.

Various tests are carried out on varnished surfaces, one of them being the pendulum hardness test. Pendulum hardness (PH) is widely used in the coating industry [Marrion 2004]. Because the pendulum method can distinguish small changes in coating hardness [Choi and Kim 2006], it is an effective method to examine curing processes of coatings [Huang et al. 2014]. The pendulum method evaluates stiffness by measuring the damping time of an oscillating pendulum. The pendulum rests on a plating surface with two steel balls. When initiated, the viscoelastic behaviour of the coating determines its release time. Hard coatings exhibit long release times.

A PH tester can be equipped with a "König" or "Persoz" pendulum. In the König method, the ball has a weight of 200 g and a diameter of 5 mm, and deflection starts at 6° and ends at 3° with an oscillation period of 1.4 seconds (reference: glass damping, 250 s). In the Persoz method, the ball has a weight of 500 g and a diameter of 8 mm, and deflection starts at 12° and ends at 4° with 1-second oscillations (reference: glass damping, 430 s) [Schwalm 2007].

In the literature there are studies on pendulum hardness (PH) values determined on various varnish types (UV system, $WBV_{One\text{-}Comp.}$ and $WBV_{Two\text{-}Comp.}$, polyurethane, synthetic, cellulosic, acrylic, etc.) applied to the surfaces of wood from different species. Some examples of such studies are described below.

Peker [1997] applied synthetic and polyurethane varnish to Scots pine and Anatolian chestnut wood surfaces treated with tanalith-CBC (13%) and paraffin + synthetic thinner + varnish (1% + 79% + 20%). The surfaces of the test samples were placed at an angle of 45° to receive the sun directly. Polyurethane varnish produced the best PH values (Scots pine 100%, chestnut 85%), followed by synthetic varnish and added water repellents.

Ozen and Sonmez [1999] applied synthetic, cellulosic, polyurethane, and acid-hardened varnishes to beech, Scots pine, oak, and chestnut woods. They then exposed the varnished materials to natural aging for 22 months. Their results showed that the PH values increased.

Yalınkılıç et al. [1999] investigated the outdoor weathering performance (6 and 9 months) of chestnut and Scots pine with alkyd-based synthetic and polyurethane varnishes applied over CCB-impregnated, water-repellent solutions, and without impregnation. It was reported that PH values increased with increasing aging time for both varnish types.

Pelit [2007] compared the effects of hardness on single and double water--based varnishes applied to the surfaces of Scots pine and Eastern beech woods with different moisture contents (8%, 10%, and 12%). The results showed that for both wood species, the PH values for $WBV_{One-Comp.}$ were higher than those for $WBV_{Two-Comp.}$.

Cakicier [2007] determined the performance properties of the varnish layer after weathering using a xenon-arc lamp, on Scots pine, iroko, and Anatolian chestnut test samples coated with $WBV_{One-Comp.}$ and $WBV_{Two-Comp.}$.

Pelit [2014] determined the PH values of $WBV_{One-Comp.}$ and $WBV_{Two-Comp.}$ applied to beech and Scots pine woods that had been heat-treated at 190 ℃, 200℃, and 210℃ for 2 h.

In a study by Cakicier et al. [2017], synthetic varnish and $WBV_{One-Comp.}$ were applied to European alder, American ash, white poplar and white willow wood samples after heat-treatment at 190℃ for 1.5 h and at 212℃ for 2 h (ThermoWood). The coated specimens were exposed to a UV-A 340 nm fluorescent lamp in a QUV accelerated weathering tester for 144, 288, and 432 h. They reported that the PH values varied depending on the weathering time.

Ulay [2018] investigated the values of PH after weathering in iroko and ash woods coated with different ($WBV_{One-Comp.}$ and $WBV_{Two-Comp.}$, two-component solvent-based acrylic and polyurethane) varnishes and heat-treated at 190°C for 1.5 h and at 212°C for 2 h. The varnished materials were exposed to aging for 144, 288, 432 and 576 h in a QUV accelerated aging test device with UV-B 313 EL fluorescent lamps. The results showed that the PH value decreased.

Gunduz [2018] treated Scots pine wood with 3% aqueous solutions of Wolmanit CX-8, Celcure AC-500 and Adolit KD-5. Later, water-based, polyurethane, and cellulosic varnishes were applied. The varnished materials obtained were exposed to aging for 250, 500, 750, and 1000 h. According to the results, for all three varnish types, the pre-impregnation process before varnishing led to improvement in the surface hardness values of test samples.

Kilic [2019] carried out research on weathered and unweathered (in tangential and radial section directions) sessile oak, Scots pine, and chestnut wood coated with polyurethane, water-based, and acrylic varnishes. Higher PH values were obtained for oak and chestnut than for Scots pine.

Aykaç and Sofuoğlu [2021] applied synthetic, cellulosic, water-based, and polyurethane varnishes to bamboo surfaces, and reported the PH values as 11.40, 18.93, 23.67, and 60.06, respectively.

Baysal et al. [2021] found the PH value of water-based varnish layers applied to Calabrian pine wood to be 45.00 after 6 months of outdoor conditions, compared with 28.60 in the case of unaged samples.

Today, it can be observed that there are few studies on the aging performance of heat-treated wood material surfaces after varnish application. In

this research, materials were produced from Scots pine, Eastern beech, and sessile oak woods which had been heat-treated by the ThermoWood method at 190°C for 2 h and 212°C for 1 and 2 h, and $WBV_{One-Comp.}$ and $WBV_{Two-Comp.}$ were applied. In the QUV aging device, samples were exposed to UV-A 340 lamps for 144, 288, and 432 h. After aging, PH values were determined. As can be seen from the literature review, no study of this type has previously been carried out. It is thought that the information obtained will contribute to explaining the relationship between wood type, heat treatment, water-based varnish, and aging, and provide information to the relevant industries [Ayata 2014].

Materials and methods

Wood materials

Scots pine (*Pinus sylvestris* L.), Eastern beech (*Fagus orientalis* Lipsky), and sessile oak (*Quercus petreae* L.) woods were selected for this study. Scots pine wood is used as a veneer board and in the plywood, furniture, mine post, wire post, sleeper, fibre, chipboard, and paper industries [Bozkurt and Erdin 2000]. Eastern beech wood is used in solid furniture, bent furniture, sports equipment, tool handles, turning, plywood, veneer, parquet, barrels, bodywork, chips, fibres, and paper wood [Bozkurt 1992]. Sessile oak wood is used as a solid wood in furniture, small shipbuilding, docks, ports, in-water constructions, wagon construction, and all kinds of use involving contact with soil, as well as in high-quality carpentry work, carving, parquet, body making, and cutting of veneer boards in furniture and panelling [Bozkurt and Erdin 2000].

Heat treatment application

The wood materials were heat-treated at 190°C for 2 h and at 212°C for 1 and 2 h, according to the ThermoWood® method, at the Novawood Factory in Gerede, Bolu, Turkey [Anonymous 2003]. After heat treatment, the timbers were kept in an air conditioning room with an average temperature of 20 ±2°C and 65 ±5% relative humidity according to the TS 642 ISO 554 [1997] standard. Then, samples were sanded with 100, 120, and 180 grit sandpaper in a calibrated sanding machine in accordance with recommendations for industrial applications.

Application of water-based varnishes

Samples were brought to a clean size of 500 × 100 × 14 mm before varnishing, and were sanded again with 180 grit sandpaper. To the heat-treated Scots pine, beech, and oak timber, AQUACOOL FX 6150 biocide and lignin preservative containing colourless primer, obtained from the Dual Paint Company and prepared for application according to the manufacturer's recommendations, were

applied in two layers with a dipping period of 10 seconds. After waiting for 3 h at 20°C ambient temperature between layers, the dried varnish film was sanded with 400 grit water sandpaper, and the second layer was applied after removal of dust. The primer layer, which was fully dried, was sanded with 400 grit water sandpaper, dust was removed, and $WBV_{One-comp.}$ and $WBV_{Two-comp.}$ topcoat varnish applications were performed. AQUACOOL FX 7680/00 exterior colourless topcoat varnish from the Dual Boya Company was used in the topcoat application ***one-component water-based varnish*** $(= WBV_{One-comp.})$. AQUACOOL 0820/00 Exterior colourless topcoat varnish (varnish + AQUACOOL AX 0115 hardener (25%) + water (10%)) from the Dual Boya Company was used in the final coat of the ***two-component water-based varnish*** $(= WBV_{Two-comp.})$ application. Table 1 gives information on the application of $WBV_{One-comp.}$ and $WBV_{Two-comp.}$ according to recommendations for industrial applications [Ayata 2014].

Table 1. $WBV_{One-comp.}$ and $WBV_{Two-comp.}$ application

	Varnish type	Number of layers	Application amounts by solid	
$WBV_{One-comp.}$	FX 6150 UV protective primer immersion method (solid matter 19.45%)	1	130 g/m^2	25 g/m^2
		2	70 g/m^2	13 g/m^2
	Total solid matter for FX 6150 UV →			**38 g/m^2**
	FX 7680 finish coating method with pistol (solid matter 43.26%)	1	140 g/m^2	61 g/m^2
		2	140 g/m^2	61 g/m^2
	Total solid matter for FX 7680 →			**122 g/m^2**
	Total solid matter for FX 6150 UV + FX 7680 (38 + 122) →			**160 g/m^2**
$WBV_{Two-comp.}$	FX 6150 UV Protective Primer Immersion method (solid matter 19.45%)	1	130 g/m^2	25 g/m^2
		2	70 g/m^2	13 g/m^2
	Total solid matter for FX 6150 →			**38 g/m^2**
	FX 0820 2K finish coat method with pistol (solid matter 37.78%)	1	105 g/m^2	40 g/m^2
		2	105 g/m^2	40 g/m^2
		3	105 g/m^2	40 g/m^2
	Total solid matter for FX 0820 2K →			**120 g/m^2**
	Total solid matter for FX 6150 + FX 0820 2K (38 + 120) →			**158 g/m^2**

A top-chamber spray gun with a gun tip opening of 2.0 mm was used. According to the recommendations for industrial surface application, the sample was moved parallel to the surface at a distance of 20-25 cm from the spray gun, and cross-layer application was performed on each layer, first perpendicular to

the fibres and then parallel to the fibres. The application air pressure was 2 bar. After applying the first layer of varnish, the sample was left to dry for 3 h at 20°C ambient temperature, the dried layer was sanded lightly with 400 grit water sandpaper, and the second layer was applied. The sample was then again left for 3 h at 20°C ambient temperature, the dried layer was sanded lightly with 400 grit water sandpaper, and the third layer was applied. Care was taken to ensure that the film layer thicknesses were equal to each other, according to the proportions of the solid matter contents of varnishes given in Table 5.

Some technical features of the colourless filler and $WBV_{One-comp.}$ and $WBV_{Two-comp.}$ supplied as a set by the manufacturer are given in Table 2 [Ayata 2014].

Table 2. Manufacturer's information about the varnishes applied

Varnish type	Ingredients	Density	PH value	Solid matter (%)	Viscosity
FX 6150 UV protective primer	Acrylic resin, biocide and UV protection	1.02	9.2	19 ±2	11 seconds at 20°C in DIN 4 cabinet
FX 7680 outdoor bright lacquer	Acrylic and aliphatic PU resin	1.05	9.3	42 ±2	45-55 seconds at 20°C in DIN 6 cabinet
FX 0820 outdoor bright lacquer 2K	Aliphatic PU dispersion	1.03	8.5	32 ±2	45-55 seconds at 20°C in DIN 6 cabinet
AX 0115 hardener	45–55 seconds at 20°C in DIN 6 cabinet	–	–	66-72	–

Artificial weathering

After $WBV_{One-comp.}$ and $WBV_{Two-comp.}$ were applied to experimental samples of Scots pine, beech, and oak wood, they were left to dry for three weeks in an air conditioning laboratory at 20 ±2°C at 12% humidity and 65 ±3% relative humidity. Then the varnished materials prepared by modifying the aging environment conditions of the ASTM G 154-06 [2006] standard (15 minutes water spray, 8 h UV; 0.67 light intensity, 18 minutes water spray, 2 h UV and 50 °C ambient temperature) were exposed to UV-A 340 fluorescent lamps in a QUV accelerated weathering tester. They were exposed to UV aging effects for 144, 288 and 432 h [Ayata 2014].

Determination of solids

Following the principles of ASTM D 1644-01 [2006], the varnishes were placed in a concave clock glass of Ø 75 ±5 mm, whose tare had been previously taken,

with a dropper rate of 2 ±0.2 g, then kept in an oven at 60°C until the weight became stable. Solvents were completely evaporated and re-weighed [Ayata 2014]. Solid amounts were calculated using the following formulae:

$$Km = \frac{Vu - Cb}{Vu} \cdot 100 \tag{1}$$

$$Vu = G - D \tag{2}$$

$$Cb = G - E \tag{3}$$

where Vu = varnish applied (g), Cb = evaporating solvent (g), Km = solid matter (%), G = wet weight (g), D = tare (g), and E = dry weight (g).

Determination of impregnation retention rates

A short-term impregnation dipping method was used in the application of AQUACOOL FX 6150 colourless primer varnish, which was prepared for application according to the manufacturer's recommendations, and test samples were placed in the impregnation material 2 times for 10 seconds. The amount of solution absorbed and net dry matter content of the impregnated samples were calculated using the following formulae, according to the TS 5723 [1988] standard [Bozkurt et al. 1993; Ayata 2014]:

$$\text{Retention} = \frac{G \cdot C}{V} \cdot 10 \, \text{kg/m}^3 \tag{4}$$

$$\text{Retention} = \frac{\text{Moes} - \text{Moeö}}{\text{Moeö}} \cdot 100 \tag{5}$$

where G = amount of solution absorbed by sample ($m_1 - m_0$) (g), m_0 = weight before impregnation (g), m_1 = wet weight after impregnation (g), C = solution concentration, V = volume of wood sample (cm^3), Moes = complete dry weight of sample after impregnation (g), and Moeö = full dry weight of sample before impregnation (g).

Dry layer thickness measurement

Dry film layer thicknesses of varnishes were determined in a PosiTector 200 device in accordance with principles specified in the ASTM D 6132 [2008] standard.

Determination of pendulum hardness

Pendulum hardness values were obtained in accordance with the principles specified in ANS/ISO 1522 [1998], using the König method with a PH tester. The device determines layer hardness according to abnormalities of a pendulum oscillating with two balls with hardness of 63 ±3.3 HRC and diameter 5 ±0.0005 mm on the surface of a sample placed on the sample platform. After the test, the samples, which were fully dried, were conditioned for 16 h at

$23 \pm 2°C$ and $50 \pm 5\%$ relative humidity in accordance with the principles specified in ANS/ISO 1522 [1998] [Ayata 2014].

Statistical analysis

Homogeneity groups, minimum and maximum values, standard deviations, means, analysis of variance, and LSD (least significant difference) critical values were determined using the MSTATC statistical program.

Results and discussion

Results for the solid matter contents of the varnishes used in the study are shown in Table 3. The lowest solid content (19.45%) was obtained for the impregnated colourless filler varnish FX 6150, and the highest (43.26%) for $WBV_{One-Comp.}$.

Table 3. Solid contents of the varnishes used

Varnish type		Solid content (%)
Impregnated Filler Colourless FX 6150 UV	→	19.45
$WBV_{One-comp.}$ (FX 7680)	→	43.26
$WBV_{Two-comp.}$ (FX 0820 2K + AX 0115 Hardener)	→	37.78

Retention rates of Scots pine, beech, and oak woods heat-treated according to the ThermoWood method are shown in Table 4. After a 2×10-second impregnation process applied to heat-treated wood materials the highest net dry matter and retention rate were obtained for the Scots pine sample heat-treated at 212°C for 2 h, and the lowest for the beech sample heat-treated at 190°C for 2 h. It was determined that the net dry matter and percentage retention increased with increasing heat treatment time and temperature (Table 4) [Ayata 2014].

Table 4. A: Net dry matter and B: Retention

Heat treatment	Scots pine		Beech		Oak	
	A (kg/m³)	B (%)	A (kg/m³)	B (%)	A (kg/m³)	B (%)
190°C for 2 h	9.8089	10.34	6.2698	4.09	6.5139	4.57
212°C for 1 h	12.2580	11.86	6.8494	4.94	6.6969	5.20
212°C for 2 h	12.9515	14.05	7.5817	5.41	6.8342	5.25

Table 5 shows measurement results for the dry film thickness of $WBV_{One-comp.}$ and $WBV_{Two-comp.}$. The highest layer thickness was obtained for oak heat-treated at 212°C for 2 h and varnished with $WBV_{Two-comp.}$, and the

lowest for beech wood heat-treated at 212°C for 1 h and varnished with $WBV_{One-comp.}$ [Ayata 2014] (Table 5).

Table 5. Dry film thickness (µm) (*: Highest value, **: Lowest value)

Heat treatment	Varnish type	Scots pine	Beech	Oak
190°C for 2 h	$WBV_{One-comp.}$	139.80	137.00	142.00
	$WBV_{Two-comp.}$	155.00	152.00	153.80
212°C for 1 h	$WBV_{One-comp.}$	140.80	**136.40****	147.00
	$WBV_{Two-comp.}$	155.40	151.80	156.60
212°C for 2 h	$WBV_{One-comp.}$	144.00	139.00	148.60
	$WBV_{Two-comp.}$	154.60	152.40	**158.20***

PH values were found to differ according to the wood type, heat treatment, varnish type, and aging period. Multiple analysis of variance (ANOVA) was performed to determine which factor caused this variation, and the results are given in Table 6. According to the ANOVA results, the factors of wood type, heat treatment, varnish type, aging period, and mutual interactions of these factors were found to be significant ($\alpha = 0.05$).

Table 6. Results of analysis of variance

Source	DF	Sum of squares	Mean square	F	Sig.
Wood Type (A)	2	17301.211	8650.606	1174.1182	0.0000*
Heat Treatment (B)	2	2243.353	1121.676	152.2414	0.0000*
Interaction (AB)	4	4245.639	1061.410	144.0616	0.0000*
Varnish Type (C)	1	578170.012	578170.012	78473.1098	0.0000*
Interaction (AC)	2	10950.233	5475.117	743.1195	0.0000*
Interaction (BC)	2	2659.008	1329.504	180.4492	0.0000*
Interaction (ABC)	4	2888.783	722.196	98.0213	0.0000*
Weathering Period (D)	3	111164.849	37054.950	5029.3461	0.0000*
Interaction (AD)	6	1387.122	231.187	31.3783	0.0000*
Interaction (BD)	6	4967.914	827.986	112.3798	0.0000*
Interaction (ABD)	12	3735.828	311.319	42.2543	0.0000*
Interaction (CD)	3	7416.782	2472.261	335.5518	0.0000*
Interaction (ACD)	6	1642.256	273.709	37.1497	0.0000*
Interaction (BCD)	6	2111.081	351.847	47.7550	0.0000*
Interaction (ABCD)	12	3134.794	261.233	35.4563	0.0000*
Error	648	4774.300	7.368		
Corrected Total	719	758793.165			

*: Significant at the level 0.05, DF: degrees of freedom

Results of the Duncan comparison test performed at the levels of wood type, heat treatment, varnish type, and aging period are given in Table 7. According to the results at the level of wood species, the PH value was highest for oak and lowest for Scots pine. At heat treatment level, the highest PH value was found for samples heat-treated at 190°C for 2 h, and the lowest for samples heat-treated at 212°C for 2 h. At the level of varnish type, the highest PH was found for $WBV_{Two\text{-}comp.}$, and the lowest for $WBV_{One\text{-}comp.}$. Finally, the highest PH value was obtained for samples exposed to 432 h of UV aging, and the lowest for unweathered samples.

Table 7. Duncan test results for factors

Factor		Average	*HG*	LSD
Wood type	Scots pine	59.65	C**	
	Beech	68.52	B	+ 0.4866
	Oak	71.09	A*	
Heat treatment	190°C for 2 h	68.02	A*	
	212°C for 1 h	67.28	B	+ 0.4866
	212°C for 2 h	63.96	C**	
Varnish type	$WBV_{One\text{-}Comp.}$	38.08	B**	
	$WBV_{Two\text{-}Comp.}$	94.76	A*	+ 0.3973
Weathering period	Unweathered	46.09	D**	
	144 h	74.51	B	
	288 h	66.88	C	+ 0.5618
	432 h	78.19	A*	

HG: Homogeneity Group, *: Highest value, **: Lowest value.

The results of the Duncan test performed for the interactions of wood type, heat treatment, varnish type and aging period are given in Table 8. In addition, the changes occurring after weathering periods were calculated and are given in the Table as percentages.

The hardness values obtained for unweathered $WBV_{One\text{-}comp.}$ and $WBV_{Two\text{-}comp.}$ were close to each other. In a previous study, Cakicier [2007] also found that the PH values were close to each other in the case of unweathered specimens of wood species treated with acrylic-modified $WBV_{Two\text{-}comp.}$ and $WBV_{One\text{-}comp.}$.

In this study, the PH values of $WBV_{Two\text{-}comp.}$ were higher than those of $WBV_{One\text{-}comp.}$ on all heat-treated wood species (Table 8). A similar result was obtained in the study by Kazan [2009]. In that study, PH tests were carried out on Scots pine, beech, and chestnut woods heat-treated at 100°C, 125°C, and

150°C for 2, 4, and 6 h and coated with $WBV_{One-comp.}$ and $WBV_{Two-comp.}$. In studies by Pelit [2007] and Ulay [2018], it was reported that the PH values of $WBV_{One-comp.}$ were higher than those of $WBV_{Two-comp.}$ for the studied wood types. The opposite was observed in this study.

In this study, PH values of 20.40, 26.90, and 27.90 respectively were obtained for unweathered samples of Scots pine, beech, and oak woods heat-treated at 212°C for 2 h and coated with $WBV_{One-comp.}$, and the corresponding values for $WBV_{Two-comp.}$ were 54.00, 84.30 and 81.60. In the study by Ulay [2018], it was found that the PH values of iroko and ash woods heat-treated at 212°C for 2 h and coated with $WBV_{One-comp.}$ were 65.60 and 78.70 respectively in unweathered samples, compared with values of 51.90 and 59.80 in unweathered samples coated with $WBV_{Two-comp.}$. Peker [2015] determined the PH values of Scots pine and beech woods with water-based varnish applied to be 22.00 and 37.60 respectively. Aykaç and Sofuoğlu [2021] determined the PH value of 23.67 in a water-based varnish applied to the bamboo surface. PH values were determined as 10.80 and 11.20, respectively, in Scots pine and beech woods with water-based varnish by Goktas and Toker [2010]. Sarica [2006] reported PH values of 42.20, 37.00, 31.20, and 28.40 for water-based varnish-coated beech, sessile oak, Scots pine, and Uludağ fir, respectively. It is reported in the literature that surfaces with more oscillations are hard, while surfaces with fewer oscillations have lower hardness [Sonmez 1989]. Pelit [2014] reported that the PH values for $WBV_{One-comp.}$ and $WBV_{Two-comp.}$ applied to Scots pine and beech woods heat-treated at 190°C, 200°C, and 210°C for 2 h increased with increasing heat treatment temperature.

In this study, while the highest PH value was obtained after 144 h weathering of oak samples heat-treated at 212°C for 1 h and coated with $WBV_{Two-comp.}$, the lowest PH value was obtained for unweathered samples of Scots pine heat-treated at 190°C for 2 h and coated with $WBV_{One-comp.}$. When the unweathered and weathered samples were compared, the smallest percentage increase (16.33%) was obtained after 288 h of weathering for beech specimens varnished with $WBV_{Two-comp.}$ and heat-treated at 212°C for 1 h, while the highest percentage increase (149.25%) was found after 432 h of weathering for oak specimens varnished with $WBV_{One-comp.}$ and heat-treated at 190°C for 2 h (Table 8). Ozen and Sonmez [1999] reported that after 22 months of natural aging, differences from 66% to 288% were obtained in the PH values of varnish layers. Baysal et al. [2021] found a 57.34% increase in PH value after 6 months of exposure to outdoor conditions in water-based varnish layers applied to Calabrian pine wood. Cakicier [2007] also reported that PH values of "$WBV_{Two-comp.}$ with acrylic modified" increased in all wood species after 144 h and 288 h of aging. It was observed in the study that PH values increased with increasing weathering time.

Table 8. Results of Duncan comparison test for interactions of wood type, heat treatment, varnish type and weathering period

Heat treatment	Varnish type	Weathering period	N	Scots pine				Beech				Oak			
				mean	***%	HG	SS	mean	***%	HG	SS	mean	***%	HG	SS
190°C for 2 h	WBV One-comp.	Unweathered	10	19.30	-	d`	0.67	20.90	-	d`	1.29	20.10	-	d	0.88
		144 hours	10	41.20	113.47	`	1.32	41.50	98.56	`	1.27	43.80	117.91	Z[\]^	1.55
		288 hours	10	38.00	96.89	‾ab	1.63	45.40	117.22	‾YZ	0.97	39.50	96.52	`a	0.71
		432 hours	10	46.00	138.34	YZ	1.25	49.10	134.93	X	1.45	50.10	**149.25**	X	2.08
	WBV Two-comp.	Unweathered	10	52.60	-	VW	1.58	72.50	-	ST	1.78	82.00	-	OP	3.83
		144 hours	10	107.40	104.18	GH	2.88	98.20	35.45	K	2.78	121.50	48.17	B	3.24
		288 hours	10	90.20	71.48	M	3.82	104.50	44.14	I	0.84	117.60	43.41	C	1.96
		432 hours	10	102.90	95.63	IJ	3.18	110.80	52.83	E	3.46	117.30	43.05	C	4.42
212°C for 1 h	WBV One-comp.	Unweathered	10	21.30	-	d	0.82	21.10	-	d	1.97	20.00	-	d`	1.05
		144 hours	10	43.10	104.18	]\^_	2.02	44.80	112.32	YZ[	0.92	41.50	107.50	^`	1.18
		288 hours	10	37.40	71.48	ab	2.12	39.70	88.15	`a	2.21	44.80	124.00	‾YZ[\	0.79
		432 hours	10	46.30	95.63	Y	0.82	51.00	141.71	WX	1.56	45.50	127.50	YZ[	1.72
	WBV Two-comp.	Unweathered	10	58.70	-	U	4.72	74.10	-	RS	3.00	71.90	-	ST	6.97
		144 hours	10	98.50	67.0	K	2.27	108.20	46.02	FG	1.87	127.70	77.61	A*	3.23
		288 hours	10	79.50	35.43	Q	1.35	86.20	**16.33**	N	2.20	113.30	57.58	D	1.42
		432 hours	10	102.90	75.30	IJ	6.08	110.30	48.85	EF	4.37	126.90	76.50	A	6.05
212°C for 2 h	WBV One-comp.	Unweathered	10	20.40	-	d	0.84	26.90	-	c	1.10	27.90	-	c	0.74
		144 hours	10	43.50	113.24	[\^_	1.18	45.30	68.40	YZ\	1.42	37.80	35.48	ab	1.40
		288 hours	10	35.90	75.98	b	2.23	42.20	56.88	`	1.23	41.20	47.67	‾`	1.03
		432 hours	10	42.60	108.82	]^_	0.97	50.10	86.25	‾X	1.20	45.70	63.80	‾YZ[	0.82
	WBV Two-comp.	Unweathered	10	54.00	-	V	3.20	84.30	-	NO	3.06	81.60	-	PQ	2.55
		144 hours	10	84.10	55.74	NO	3.31	104.90	24.44	I	1.29	108.10	32.48	FG	4.18
		288 hours	10	71.60	32.59	T	3.72	101.70	20.64	J	1.42	75.20	-7.84	R	2.74
		432 hours	10	94.10	74.26	L	6.33	110.80	31.44	E	4.10	105.10	28.80	HI	4.36

LSD ±2.384, N: Number of measurements, *HG*: Homogeneity Group, *SS*: Standard Deviation, *: Highest value, ***: Change (%).

While some researchers [Yalınkılıç et al. 1999; Esser et al. 1999; Decker et al. 2004; Gunduz 2018; Ozen and Sonmez 1999; Baysal et al. 2021] have reported an increase in the PH value after weathering, in other research it has been reported to decrease [Ulay 2018]. This is likely due to the use of wood species with different anatomical characteristics and varnish types with different chemical properties.

Some authors have given explanations for the increase in hardness after aging. Decker et al. [2004] reported in their study that the hardness of UV-cured PU-acrylate varnish with water solvent applied to a 30 μm thickness increased after aging. In addition, they stated that in the degradation mechanism caused by the aging process, urethane (C–NH) bonds would be most sensitive to UV radiation. Esser et al. [1999] reported very good results for the hardness and ability to overlay of water-soluble surface coatings, which form bonds through reaction drying and cross-molecular bonds. They also found that layer hardness increased with the aging effect. Cakicier [2007] reported that there was an increase in layer hardness due to the aging effect, and there was no difference between the values obtained after aging for 144 h and 288 h. He stated that the temperature effect, which increases during the aging process, increases cross-links between varnish molecules, which leads to an increase in the hardness of polymeric layers. According to Perrin et al. [2001], using alkyd, urethane and chlorinate polymers, an increase in acidic conditions with UV aging causes hydrolysis and a decrease in hardness. Holzhausen et al. [2002] stated that physical and chemical aging creates internal stress in the structure of organic varnish/paint systems and causes an increase in fragility. In addition, they reported that the layer temperatures at which resistance to cracking was highest were 25°C, 40°C, and 60°C. They also stated that layers attained a very hard and brittle structure at temperatures of 80°C and above.

Conclusions

The following results were obtained in this study:
- Analysis of variance results showed significance for all tests.
- In this study of heat-treated wood material surfaces, it was determined that it would be appropriate to use wood preservatives in the impregnation process and apply filling varnishes according to the dipping method, with two layers of dipping, and after the impregnation process, it would be appropriate to work with 400 grit water sandpaper on the wood material surfaces.
- At the wood type level, PH value was highest in oak and lowest in Scots pine. Oak wood samples gave the highest value among samples that were heat-treated, varnished, and aged under the same conditions. This can be assumed to be due to the differences in anatomical structure between the wood species used.

- At the heat treatment level, the highest PH values were determined in samples heat-treated at 190°C for 2 h, and the lowest in the samples heat-treated at 212°C for 2 h. It was observed that the "temperature" and "time" factors in the heat treatment application have an effect on the PH value. It was found that as the temperature increased, the PH value decreased.

- At the varnish type level, the PH value was determined to be highest for $WBV_{Two-comp.}$ and lowest for $WBV_{One-comp.}$. It can be concluded that this is due to the structural properties of the resin used in the production of $WBV_{Two-comp.}$. The $WBV_{Two-comp.}$ used in the study has reaction drying properties. It is likely that the surface hardness of these varnishes is higher than that of $WBV_{One-comp.}$ due to their molecular size and molecular weight.

- At the level of weathering time, the highest PH value was determined in the samples with 432 h weathering, and the lowest in unweathered samples. Accordingly, long-term weathering increased the surface hardness of the varnish layers.

In future studies, it will be important to compare the results obtained with various aging methods (natural, xenon lamp, UV-B-313 lamp, and UV-C lamp) applied to the materials obtained by applying $WBV_{One-comp.}$ and $WBV_{Two-comp.}$ to the surfaces of heat-treated wood materials. In addition, it is important to test other wood species and different heat treatment methods which are known to be important in the furniture industry.

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