

The Effect of Bleaching Agents on Color Change in Different Section Shapes in Beech And Fir Woods

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Abstract

Aim of study: It is an investigation of the effects of bleaching processes on the color change in the wood of tree species Eastern Beech (*Fagus Orientalis Lipsky.*) and Eastern Black Sea Fir (*Abies Nordmanniana subsp.*) were used in the study. Sodium hydroxide-hydrogen peroxide, oxalic acid, peracetic acid diluted 1/3, peracetic acid diluted 1/6 were used as bleaching agents. Trial samples were prepared in accordance with standards and color change measurements were made.

Area of study: Surface treatments on wooden materials

Material and methods: In the study, two wood species and one varnish type were used; Color changes were tested by applying various bleaches to the wooden material by rubbing method.

Main results: As a result of the study, differences were observed in all cross-section shapes in beech wood bleaching measurements with 1/6 diluted peracetic acid, and differences were observed in cross-section shapes in fir wood bleaching measurements. The best bleaching of fir wood was achieved with peracetic acid.

Highlights: The bleaching process allows the wooden material to easily acquire a homogeneous color. Since the cell arrangements are different in different cross-sectional shapes, the bleaching rates are different from each other. While there is not much difference in the color changes in the wood material when bleached with oxalic acid, the samples are bleached as a result of bleaching with sodium hydroxide-hydrogen peroxide and peracetic acid. Significant changes have occurred in color changes. The reason for this difference is due to the different degrees of corrosion of bleaching agents.

Keywords: Bleaching, Color Change, Cross Sectional Shape, Eastern Beech, Eastern Black Sea Fir

Ağartıcı Maddelerin Kayın ve Gökmar Ahşaplarında Farklı Kesit Şekillerindeki Renk Değişimine Etkisi

Öz

Çalışmanın amacı: Ağartma işlemlerinin ağaç türlerinin odunlarında renk değişimine etkilerinin araştırılmasıdır. Çalışmada ağaç türleri Doğu Kayını (*Fagus Orientalis Lipsky.*), Doğu Karadeniz Gökmarı (*Abies Nordmanniana subsp.*) kullanılmıştır. Ağartma maddesi olarak sodyum hidroksit-hidrojen peroksit, oksalik asit, perasetik asit 1/3 seyreltilmiş, perasetik asit 1/6 seyreltilmiş ağartma maddesi olarak kullanılmıştır. Deneme numuneleri standartlara uygun olarak hazırlanmış ve renk değişimi ölçümleri yapılmıştır.

Çalışma alanı: Ahşap malzemede üst yüzey işlemleri.

Materyal ve yöntem: Çalışmada iki ağaç türü ve bir vernik türü kullanılarak; ahşap malzemenin üzerine sürme yöntemi ile çeşitli ağartıcılar uygulanarak renk değişimleri test edilmiştir.

Temel sonuçlar: Çalışma sonucunda 1/6 oranında seyreltilmiş perasetik asit kayın ağacı ağartma ölçümlerinde tüm kesit şekillerinde, gökmar ağacı ağartma ölçümlerinde ise kesit şekillerinde farklılıklar gözlenmiştir. Gökmar odununda en iyi ağartma perasetik asit ile elde edilmiştir.

Araştırma vurguları: Ağartma işlemi, ahşap malzemenin kolaylıkla homojen bir renk almasını sağlar. Farklı kesit şekillerinde hücre dizilişleri farklı olduğundan dolayı ağartma oranları birbirinden farklıdır. Oksalik asit ile yapılan ağartmada ağaç malzemede renk değişimlerinde pek farklılık olmazken, sodyum hidroksit-hidrojen peroksit, perasetik asit ile ağartma sonucu numunelerin renk değişimlerinde önemli değişiklikler meydana gelmiştir. Bu farklılığın sebebi ağartma maddelerinin aşındırma derecelerinin farklı olmasından kaynaklanır.

Anahtar Kelimeler: Ağartma, Renk Değişimi, Kesit Şekli, Doğu Kayını, Doğu Karadeniz Gökmarı



Introduction

Today, many surface treatment agents and methods have been developed for surface treatments. There are many different types of wood used in the furniture industry. Therefore, it can be estimated how complex and difficult the surface treatments are. It is very important to know for what purpose the materials used in surface treatments (wood materials, paint-varnish, etc.) will be used. Otherwise, the selection of materials and the method used will be very difficult according to the place of use. Among the important characteristic features of wood is its ability to be painted or varnished. In addition, tree species can exhibit quite different behavior when dealing with various tools or machines. For this reason, it is necessary to determine the suitability of the surface characteristic of the wood material, which is an important indicator for different areas of use (Demirkır et al., 2017). Today, bleaching is a method applied to obtain the desired color in solid wood materials. Many chemicals are used in bleaching processes, the most common ones being hydrogen peroxide and oxalic acid (Kurtoglu, 2020). Wood bleaching is a process used in the papermaking process to prevent wood mildew, prepare transparent wood. Wood bleaching methods are basically divided into oxidative bleaching and reductive bleaching (Chen et al., 2012; Xu et al., 2022; Ren et al., 2022). Sulfur dioxide, sodium bisulfite, etc. Reducing bleaching agents, such as bleach, usually works by reducing the pigments in wood. But there is a possibility that it is oxidation that causes recoloring of the wood after bleaching. It causes a decrease in the whiteness of the wood. Sodium hypochlorite, hydrogen peroxide, sodium chloride, peracetic acid, etc. oxidizing bleaches such as generally have great stability; therefore they are widely used (Lu et al., 2023). Color change has an important place in surface treatment performance. It is important to determine the color changes in the places of use, especially after the application of varnishes (Aykaç and Sofuoğlu, 2021; Budakçı et al., 2017). Many studies have been carried out for this purpose (Aytin et al 2021; Berkel, 1970; Söğütlü & Döngel 2009; Sandberg, 1999). Suleman and Rashid (1999) used various chemicals to

improve the performance of surface treatments on poplar wood. For this purpose, samples sodium hydroxide, ammonium chloride and aluminum chloride bleaching agents were used during the process. Penetration efficiency and color changes gave their values in sodium hydroxide bleach. Shakri and Seman (1995) studied the surface treatment properties of three tree species from Malaysia. In his study, he applied acid hardened, cellulosic, polyurethane varnish and glossy paint on the samples of these species and determined their hardness, abrasion, color, scratch and adhesion resistance. Akkuş and Budakçı (2020) after heat treatment to restore the natural color of the wood. They aimed to remove the discoloration on the surface of the wood by using bleaching chemicals. For this purpose, samples prepared from Scots pine (*Pinus sylvestris* L.), sessile oak (*Quercus petraea* L.), Eastern beech (*Fagus orientalis* L.) and Uludağ fir (*Abies bornmuelleriana* Mattf.) were heat treated at 300 °C. They prepared three different bleaching solutions. These ($\text{NaOH} + \text{H}_2\text{O}_2$), ($\text{NaSiO}_3 + \text{H}_2\text{O}_2$) and ($\text{H}_2\text{C}_2\text{O}_4$) were then applied to the surface of the materials at a concentration of 18%. As a result, the color change values of different solutions in different tree species decreased. In this study, the effect of bleaching processes and their effect on color changes were investigated in fir and beech woods, which have commercial importance in our country.

Materials and Methods

In this study, the materials used in the experiment are two wood species and one varnish type. The woods used were Eastern Beech (*Fagus Orientalis* Lipsky.) from the leafy tree species and Eastern Black Sea Fir (*Abies Nordmanniana* Subsp.) from the coniferous tree species. The tree species to be used in the experiments were selected from the Eastern Black Sea Region, where it spreads naturally. Trabzon, Gümüşhane and Artvin regions, where the optimal growth of the species is found, were determined as sample areas. Attention was paid to the selection of tree species from homogeneous stands and wood materials were selected for the test samples according to the simple

random sampling method. Attention was paid to the following principles in the selection of trees: age, aspect, diameter, altitude and habitat, the trees that will be the test specimens were taken care to be of smooth and solid trees with a perfect trunk structure that can best represent the environment in which they grow. The trees on which the test samples will be prepared are approximately 2.5-5.5 m. The logs of 1.20-1.50 m in length were taken from among the heights of K.T.Ü. It was brought to the Forestry Industrial Engineering laboratory of the Faculty of Forestry, and pieces of 3 cm thickness and 11 cm width with tolerance were obtained by sawing with a band saw machine, in tangential-radial sections with heartwood. Then, these pieces were stacked in a well-ventilated place and left to dry naturally. The parts with natural drying were kept in the air-conditioning room at 20 ± 2 C temperature and $65 \pm 5\%$ relative humidity until they reached a constant weight and their humidity was ensured to be approximately 12%. A total of 120 samples, 60 of each from beech and fir wood, were used. The parts whose air-conditioning processes were completed were processed in planer, thickness and circular saw machines and were brought to the dimensions of 1300x100x20 mm. The pieces were processed in a circular saw machine and cut in 3 equal pieces in the transverse direction. Then, test pieces of 400x100x20 mm were obtained, 6 from each piece. Each sample group was divided into 6 groups in order to investigate the effect of the bleaching agent. One of these groups was left as a control, and the bleaching agents mentioned above were applied to the others with a brush, with 120-150 gr m². After the application, they were kept for 1 day and then the sample surfaces were wiped with pure water with a warm cloth and cleaned of bleach residues. Then varnish was applied. Specific gravity of eastern beech is 0.68 g/cm³; the eastern black sea fir is 0.46 g/cm³. The trees used in the study were determined according to the TS 4176 standard. The radial and tangential cutting plans of the samples are given in Figure 1.

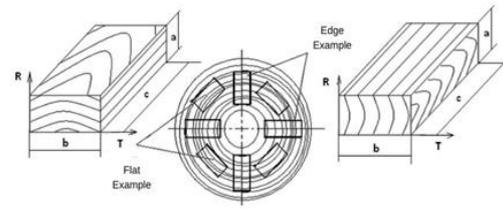


Figure 1. Flat and Edge cut plans of samples

In the research; A single varnish type was chosen, which is cellulosic based, which is widely used. Some properties of the cellulosic varnish used in the study are as follows. Density 0.95 (gr/cm³), viscosity DIN/CUP4 300 sec, powder dry (min) 3-5, to touch dry (min) 10, sandpaper dry (min) 2-4, solid amount 30%. Color protection of wood material cannot be achieved with bleaching agents alone. Therefore, cellulosic varnish was used in the study (Sönmez, 1989). In this study, 5 different bleaching agents were used and they were coded as in Table 1 below.

Table 1. Bleaching agents

Bleaching Agents	Shortening Preparation Recipe
Sodium hydroxide-hydrogen peroxide	SH-HP 35% hydrogen peroxide and 50 g hydrogen peroxide were dissolved in 1 liter of sodium hydroxide water.
Oxalic acid	OA 100 g of oxalic acid was dissolved in 1 liter of water.
Peracetic acid	PA 40% H ₂ O ₂ and 96% acetic acid were mixed in 1/1 ratio. It is a mixture of equal parts of acetic acid (CH ₃ COOH), hydrogen peroxide and water.
1/3 diluted peracetic acid	1/3 PA 1/3 ratio diluted.
1/6 diluted peracetic acid	1/6 PA 1/6 ratio diluted.

Determination of Optical Properties

The standard used in color measurements is ASTM D 2244. The color measuring head of the device uses 45° illumination and 0° angle geometry. The measuring head is suitable for glossy surfaces. However, extremely glossy surfaces may cause errors

in measurement. Because most of the light will be reflected at an angle of 45° and thus will not enter the optical fiber cable (Anonymous 2009). The CIELAB color space is used to determine the color of coated objects. It was realized with 8 separate measurements for each sample Color evaluations were carried out by calculating L*, a* and b* CIELAB coordinates with the system proposed by CIE (Commission International de l'Eclairage) in 1971 for the paper industry.. The 3-dimensional color space consists of three perpendicular axes. Obtained colors are shown with L, a and b numerical values. Here L denotes lightness from 0% (black) to 100% (white), a from green (-a) to red (+a) and b from blue (-b) to yellow (+b). The color plane is given in Figure 2.

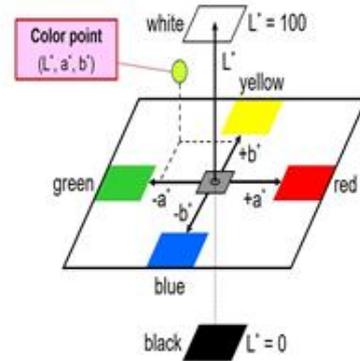


Figure 2. CIE L*a*b* Color Plane (Beetsma, 2020)

Results and Discussion

Color changes of samples as a result of bleaching processes. Color change in fir wood as a result of bleaching processes. A total of 64 sample trees, 32 of which belong to tree species, were used. The color changes obtained in the test samples after the bleaching processes of the fir wood are given in Table 2.

Table 2. Color change in fir wood after bleaching

	SAPWOOD				HEARTWOOD				
	Flat Grain	Flat Grain*	Edge Grain	Edge Grain*	Flat Grain	Flat Grain*	Edge Grain	Edge Grain*	
SH-HP	L	84.92	83.15	81.47	86.38	82.54	80.75	80.61	76.06
	a	3.36	2.09	4.48	0.64	4.29	2.71	5.77	3.88
	b	22.39	20.79	20.73	20.59	20.98	22.17	21.56	23.29
	Δ								
	E		2.71		6.24		2.68		5.23
OA	L	85.15	84.11	84.97	82.65	80.69	80.97	81.61	79.97
	a	3.78	5.28	3.58	5.56	5.96	6.11	5.01	6.82
	b	21.69	21.53	19.42	20.29	22.17	20.67	20.81	22.17
	Δ								
	E		1.84		3.18		1.54		2.79
PA	L	84.89	87.79	83.16	84.51	82.34	84.74	80.23	79.16
	a	3.82	2.05	4.53	3.63	4.69	3.44	5.59	4.98
	b	21.49	22.68	23.03	22.94	21.42	23.53	21.19	25.39
	Δ								
	E		3.61		1.64		3.45		4.39
1/3PA	L	84.83	87.47	82.55	86.82	79.15	85.99	80.86	84.38
	a	3.91	2.08	4.58	2.41	6.63	2.78	5.39	3.61
	b	22.05	21.88	20.32	23.49	22.56	22.63	19.83	21.34
	Δ								
	E		3.24		5.75		7.87		4.24
1/6PA	L	85.35	87.41	84.46	87.51	80.75	85.44	73.09	80.31
	a	3.56	2.31	3.88	2.36	4.73	3.27	7.89	4.68
	b	21.19	21.72	20.74	21.13	20.19	22.08	26.39	23.76
	Δ								
	E		2.48		3.44		5.27		8.29

*: change relative to control

The color changes obtained in the test samples after bleaching in beech wood are given in Table 3.

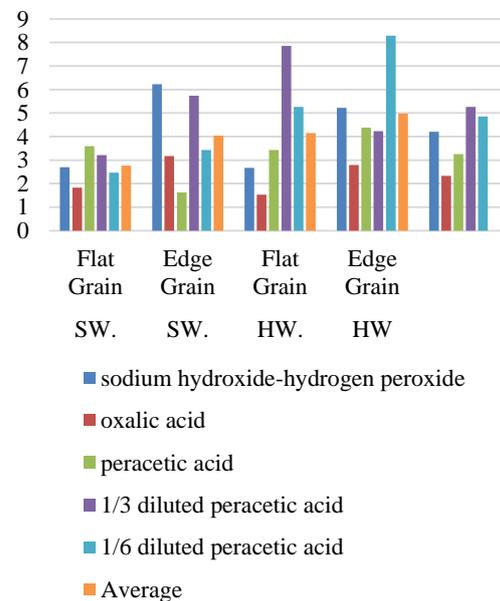
Table 3. Color change in beech wood after bleaching

		SAPWOOD				HEARTWOOD			
		Flat Grain	Flat Grain*	Edge Grain	Edge Grain*	Flat Grain	Flat Grain*	Edge Grain	Edge Grain*
SH-HP	<i>L</i>	70.79	88.59	70.83	84.69	71.44	88.49	63.89	78.37
	<i>a</i>	10.17	0.09	10.64	1.68	10.69	0.67	11.85	3.51
	<i>b</i>	25.59	14.55	24.33	14.87	26.26	13.61	24.81	18.92
	ΔE		23.26		19.03		23.49		17.72
OA	<i>L</i>	71.25	69.23	72.83	71.25	69.08	68.59	69.77	69.27
	<i>a</i>	11.09	13.45	10.14	11.87	11.68	13.07	11.28	12.32
	<i>b</i>	26.88	27.36	23.72	23.74	27.13	26.06	26.37	24.84
	ΔE		3.15		2.35		1.83		1.93
PA	<i>L</i>	71.79	76.99	73.75	77.04	72.55	77.41	69.63	76.35
	<i>a</i>	10.59	7.72	9.04	6.98	10.16	7.36	11.54	8.06
	<i>b</i>	25.61	25.38	22.61	23.13	25.48	23.82	26.39	24.69
	ΔE		5.96		3.92		5.86		7.77
1/3PA	<i>L</i>	71.24	80.29	71.53	77.29	68.66	76.41	67.02	74.69
	<i>a</i>	10.74	6.52	9.78	6.84	11.61	7.79	11.87	8.45
	<i>b</i>	25.47	25.18	23.38	23.31	27.39	26.15	26.41	26.49
	ΔE		9.99		6.48		8.74		8.5
1/6PA	<i>L</i>	72.09	81.51	75.54	82.22	68.39	77.09	67.96	78.09
	<i>a</i>	9.95	5.88	7.77	4.94	11.56	7.22	11.17	7.09
	<i>b</i>	24.31	24.29	20.48	22.02	27.06	25.42	24.79	25.16
	ΔE		10.27		7.43		9.87		10.95

*: change relative to control

Color Change in Fir Wood as a Result of Bleaching Processes

In the study of Atar et al. (2019), the effect of heat treatment on the color change of varnished wood material was investigated and they found that the lowest color change value was found in scotch pine wood material with water-based varnish and heat treatment at 165/2 °C/Hour. Chou et al. (2008) determined in their study that the color stabilization of polyurethane type top surface materials is quite high. In this study, the color change values obtained after bleaching processes are given in figure 3.



(x- axis: color change ratio y-axis: bleaching agents)

Figure 3. Color change of fir wood in experimental samples (ΔE) (Sw:Sapwood, Hw: Heartwood)

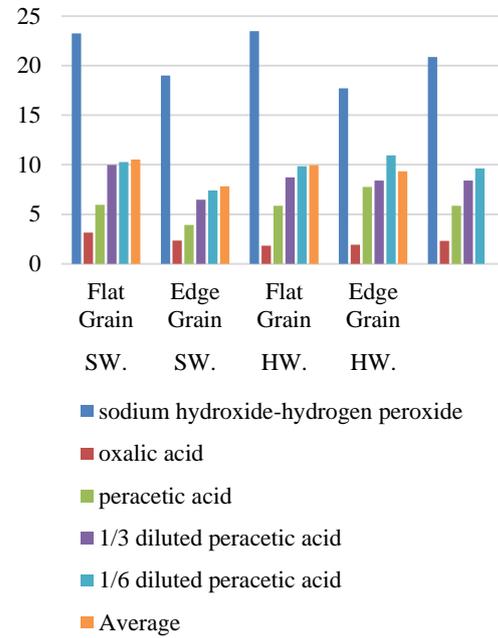
According to the results obtained, the highest color change in the flat grain of the

sapwood was obtained by bleaching with peracetic acid (3.61). The lowest was obtained after bleaching with oxalic acid (1.84). The highest color change in the edge grain of the sapwood was obtained as a result of sodium hydroxide-hydrogen peroxide (6.24) bleaching process. It was obtained as a result of bleaching with peracetic acid (1.63). The highest color change in the heartwood flat grain was obtained as a result of bleaching with 1/3 diluted peracetic acid (7.87). The lowest was obtained as a result of bleaching with oxalic acid (1.54). The highest color change in the edge grain of the heartwood was obtained by bleaching with peracetic acid (8.29) diluted at a ratio of 1/6. It was obtained as a result of bleaching with oxalic acid (2.79).

Color Change in Beech Wood as a Result of Bleaching Processes

In their study, Söğütü and Sönmez (2013) investigated the color-changing effect of UV rays on wood materials of some species treated with oil, wax and varnish. According to the results of the research, oil, wax and varnish could not protect the color of wood materials against UV rays. The least color change was obtained in liquid paraffin. Çakıcıer and Pak (2022), in their study, doussie (*Azalia africana*), sapelli (*Entandrphragma cylindrocum*), walnut (*Juglans regia*), sessile oak (*Quercus petraea* L.), iroko (*Chlorophora excelsa*) and beech (*Fagus orientalis* Lipsky). The color parameters (L^* , a^* and b^*) and the gloss properties perpendicular and parallel to the fibers at 60° were investigated after artificial aging of 252 and 504 hours in a device with UVB-313 lamps of UV system varnished materials applied to wood species. According to the results of the research, ΔE^* values were determined to increase with the increase of aging time in UV varnished doussié, sessile oak and iroko species, while it decreased in UV varnished walnut, beech and sapele wood species. The aging application consisting of UVB-313 lamps had a modifying effect on the surface structure of the materials. Budakçı (2006) proved in her study that exposure to external environment without bleaching or coating process causes color change and this negative

effect can be reduced by bleaching. In this study, the color change values obtained after bleaching processes are given in Figure 4.



x- axis: color change ratio y-axis: bleaching agents
 Figure 4. Color change (ΔE) of beech wood in experimental samples (Sw:Sapwood, Hw: Heartwood)

The highest color change in the flat grain of the sapwood was obtained by bleaching with sodium hydroxide-hydrogen peroxide (23.26). The lowest was obtained after bleaching with oxalic acid (3.14). The highest color change in the edge grain of the sapwood was obtained as a result of bleaching with sodium hydroxide-hydrogen peroxide (19.03). if it is low, it was obtained as a result of bleaching with oxalic acid (2.35). The highest color change in the heartwood flat grain was obtained by bleaching with sodium hydroxide-hydrogen peroxide (23.49). The lowest was obtained after bleaching with oxalic acid (1.83). The highest color change in the edge grain of the heartwood is obtained as a result of bleaching with sodium hydroxide-hydrogen peroxide (17.72). It was obtained as a result of bleaching with oxalic acid (1.93). General conclusion for both fir and beech wood; the reason why hydrogen peroxide is effective in color change is that it reacts with lignin protective and lignin carbonyl groups and

conjugated double bonds (nucleophilic) in the wood material. Peracetic acid, on the other hand, changes the lignin structure (electrophilic) by reacting with the olefinic and aromatic parts of lignin. For this reason, very large lignin masses such as wood and mechanical pulp can cause darkening, let alone lightening. Peracetic acid also reacts with the hexauronic acid groups of hemicelluloses. This also explains the development of color values with the dilution of the peracetic acid ratio (Cheumani-Yona, 2015).

Conclusions

Bleaching wood with chemicals means cutting off the sharing of electrons responsible for color. Bleaching provides a homogeneous color of wood material easily. In the tangential and radial section, the participation rates of the wood material are different. The color changes due to the cell arrangement differences in the tangential and radial cross-sections and the hollow structure in the tangential and radial cross-sections differ. While the color changes of the samples were not different after bleaching with oxalic acid, there were significant changes in the color changes of the samples as a result of bleaching with peracetic acid for fir wood. For beech wood, there were significant changes in the color changes of the samples as a result of bleaching with sodium hydroxide-hydrogen peroxide. The reason why there is no difference in bleaching processes with oxalic acid. Because oxalic acid is a weak organic acid. It occurs only in two linked carboxyl groups. Since peracetic acid and sodium hydroxide-hydrogen peroxide are acids with strong abrasive properties, the color change difference is evident.

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Ethics Committee Approval

N/A

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Author Contributions

Conceptualization: Ö.B.B.; T.Ö.
Investigation: Ö.B.B.; T.Ö.; Material and Methodology: Ö.B.B.; T.Ö.; Supervision: Ö.B.B.; T.Ö.; Visualization: Ö.B.B.; T.Ö.; Writing-Original Draft: Ö.B.B.; Writing-review & Editing: Ö.B.B.; T.Ö.; Other: All authors have read and agreed to the published version of manuscript.

Conflict of Interest

The authors have no conflicts of interest to declare.

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