

## Full Length Research Paper

# The color changes on varnish layers after accelerated aging through the hot and cold-check test

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The purpose of this paper is to determine the color changes of cellulosic, polyurethane and acrylic varnish layers which were applied on the surfaces of Scots pine (*Pinus sylvestris* L.), Eastern beech (*Fagus orientalis* L.) and sessile oak (*Quercus petraea* L.) wood material after accelerated aging effects through the hot and cold-check test. For this purpose, test samples were firstly kept at  $50 \pm 5^\circ\text{C}$  temperature for 1 h, and then conditioned for 1 h in a conditioning room, later moved to  $-20 \pm 2^\circ\text{C}$  temperature keeping for 1 h according to ASTM D1211-97 standard. These processes were accepted as 1 cycle and tests were continued to 20 cycles. Then the color changes were determined by using Minolta CR-231 device of tristimulus colorimeter according to ASTM D2244-07e1 standard. It was found that most color change was determined in cellulosic, polyurethane and acrylic varnish layers on the surfaces of Scots pine (*Pinus sylvestris* L.), Eastern beech (*F. orientalis* L.) and sessile oak (*Q. petraea* L.) wood material. The endurance of the protective coating (such as paint and varnish) to external effects is limited and the lifetime of the coating is determined by the type and the severity of the effects to which it is exposed. The effect of a color change on varnish layers can determine the usefulness of the varnish. It is conjectured that especially for the manufacturers and consumers in the furniture and decoration sector, the data obtained in this study will contribute to the making up of deficiencies in the understanding of the subject.

**Key words:** Varnish, hot and cold-check test, color change, wood material.

## INTRODUCTION

As wood materials which have organic, anisotropic, hygroscopic and heterogeneous structure may experience changes in dimension, have natural defects, are prone to be damaged by insects and fungi, and are not fire resistant, they are made more durable by technically suitable usage and an appropriate set of finishing processes. The protection characteristics of the finishing processes, however, vary with respect to the material used and the method of application. The endurance of the protective coating (such as paint and varnish) to external effects is limited and the lifetime of the coating is determined by the type and the severity of the effects to

which it is exposed. Effects such as humidity, hotness-coldness and abrupt temperature changes which cause degradation in the protective coating also lead to problems such as loss of brightness, color change, cracking and flaking (Sonmez and Kesik, 1999). This phenomenon reduces the lifetime and the esthetic value of especially wooden furniture and decoration elements.

It has been noted in the literature that in order to prevent cracking in the varnish layers, non-drying herbal oils, monomeric chemicals with high boiling points and polymeric resins can be used as plastifiers and that among these substances, phthalates, sebacates and phosphates are durable in the range  $69 - 70^\circ\text{C}$  (Payne, 1965). Moreover, the highest amounts of brightness loss after accelerated aging of varnish layers through the hot and cold-check test have been observed in cellulosic varnish and beech wood (Sonmez and Kesik, 1999). It has also

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been reported that when Gubas (*Endospermum peltatum* Merr.) wood material is subjected to the hot and cold-check test by applying to its surface, varnish with acidic hardener and cellulosic varnish, the surface with cellulosic varnish exhibits fracture, cracking and color change (Yolanda, 1998). The high energy of the ultraviolet (UV) rays in the sunlight causes degradation in the varnish and paint layers, and leads to surface heating with temperature rising up to 100°C or more (Feist, 1984). The energy in these rays can break the C-C, C-N and C-O bonds, and effects such as humidity and temperature change degrade the layer performance (Rosenqvist and Lingberg, 1983). According to another study, when weathered, wood material experiences discoloration, the preservatives used in the finishing processes become degraded and it becomes harder to obtain better results when the finishing processes are reapplied (Miniutti, 1964; Hon and Chang, 1984; Williams et al., 1990). In studies about making varnish layers more enduring towards external effects, it has been found that the lifetime of the silicon-resin-modified layers is 2 years, whereas that of the linseed-oil-modified layers is 5 years (Black and Mraz, 1976). The color changing effect of UV rays on some wood types processed with teak oil, liquid paraffin and shellac has been investigated and it has been observed that the oil, wax and finish cannot preserve the color of the wood materials against the UV rays, and the smallest color change occurs in the liquid paraffin case (Sogutlu and Sonmez, 2006). Another study shows that temperature or UV rays cause discoloration in wood materials and this discoloration occurs in gray, yellow, red or brown color tones, depending on the wood type (Sandermann and Schlambom, 1962; Tolvaj and Faix, 1995). Among environmental factors, UV rays are the major cause of degradation in the structure of wood materials (Futo, 1974; Ayadi et al., 2003). When cellulosic, synthetic, polyurethane and acidic-catalyst-bearing types of varnish were applied on oak, Eastern beech, chestnut and Scots pine woods, the largest color change was observed on the samples with synthetic varnish (Sonmez, 1997). On the other hand, it has been reported in another study that in the case of degradation in the protective coating, the UV rays and the water impinging on the surface play an important role in the destruction of the lignin-hemicellulose in the cell wall, this destruction causes the color of the wood material to change and the first stage of this change is the degradation of the lignin (Sudiyani et al., 2003; Mitsui, 2004). It has been noted that the amines in solvent-based varnishes get yellow in time due to oxidation and these chemicals, which cause yellowing, are not used in water-based varnishes (Johnson, 1995).

It has been stated that in the hot-cold aging tests of the varnish layers, the samples should be kept in the temperatures of -20 and 50°C for 1 h each, this process should be considered 1 period; the performance of those

layers with no degradation in 10 periods should be considered sufficiently good while layers with no degradation in 25 periods should be considered high-performance (Payne, 1965).

From this standpoint, the purpose of this study is to determine the color changes on the cellulosic, polyurethane and acrylic varnish layers applied on Scots pine (*Pinus sylvestris* L.), Eastern beech (*Fagus orientalis* L.) and sessile oak (*Quercus petraea* L.) wood material surfaces after accelerated aging through the hot and cold-check test. It is conjectured that especially for the manufacturers and consumers in the furniture and decoration sector, the data obtained in this study will contribute to the making up of the deficiencies in the understanding of the subject.

## MATERIALS AND METHODS

### Wood material

The types of wood used for the preparation of the samples in this study were Scots pine (*P. sylvestris* L.), Eastern beech (*F. orientalis* L.) and sessile oak (*Q. petraea* L.). The samples were prepared from the sapwood parts of the randomly chosen first-class timbers; they were chosen to be regular-fiber, knotless, crack-free, exhibiting no variation in color or density and to have annual rings perpendicular to the surface, with regard to the principles in TS 2470 (1976) and ASTM D358-98 (2006). The samples were cut as drafts with dimensions 110 × 110 × 12 mm and kept in an air-conditioning room with temperature 20 ± 2°C and relative humidity 65 ± 3% until they reach a non-changing weight (TS 2471, 1976). The samples were then dimensioned to be of size 100 × 100 × 10 ± 1 mm and the finishing was done first with 80-grid (on Norton scale) sandpaper and then with 100-grid sandpaper. Prior to varnishing, the sandpapered surfaces were cleaned with a soft bristle brush by means of vacuuming.

### Varnish

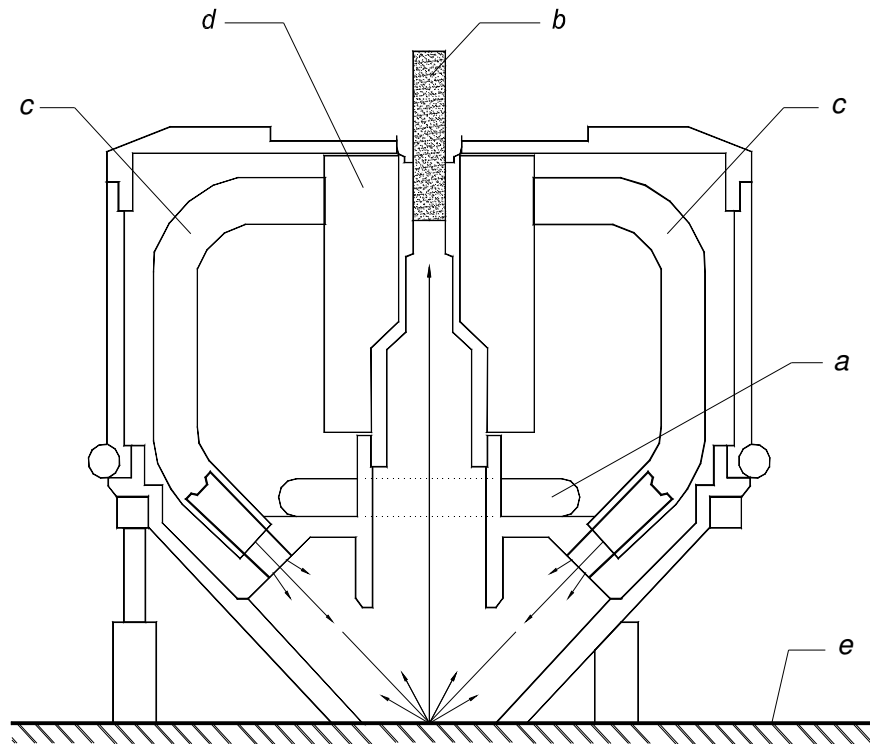
For the varnishing of the samples, in addition to a cellulosic varnish, two-part polyurethane and acrylic varnishes were used. The preparation of the varnishes for the application conditions was made with regard to the recommendations of the manufacturer firms and the principles in ASTM D3023-98 (2003), and in a way that would not negatively affect the layer performance. Table 1 lists some properties of the varnishes. Varnish application was made according to the dry-wet method with 1 filling layer followed by 2 topcoats (bright). The samples were first undercoated by the filling varnish pertaining to each system, the drying filling layers were then slightly sandpapered with 220-grid sandpaper and, after the removal of the dust, the topcoat varnish was applied. The waiting time between the layers was 24 h. The amount of applied varnish was determined by an analytical balance with a sensitivity of 0.01 g. The application was performed by a spray gun.

### Hot and cold-check test and color measurement

The varnished and fully-dried samples were prepared for the experiments by being kept for 16 h in a climate control chamber with temperature 20 ± 2°C and relative humidity 50 ± 2%, in

**Table 1.** Some properties of the varnishes.

Varnish type	pH	Density (g / m <sup>3</sup> )	Solid material percentage (by weight)	Amount of varnish to be applied (g / m <sup>2</sup> )	Nozzle gap of spray gun(mm)	Air pressure (bar)
Cellulosic filling	2.9	0.955	32	120	1.8	3
Cellulosic topcoat	3.4	0.99	31	120	1.8	3
Polyurethane filling	5.95	0.98	48	120	1.8	2
Polyurethane topcoat	4.01	0.99	44	120	1.8	2
Acrylic filling	4.3	0.95	42	120	1.8	2
Acrylic topcoat	4.6	0.97	44	120	1.8	2



**Figure 1.** Color measurement device. a: Xenon arc lamp; b: fiber optic cable (for measurement); c: fiber optic cable (for light conduction); d: mixing chamber; e: experimental sample.

compliance with the ASTM D3924-80 (2005) principles. With regard to the principles of ASTM D1211-97 (2001), the samples were then kept in a drying oven with a temperature of  $50 \pm 5^\circ\text{C}$  for 1 h, conditioned in the laboratory environment for 1 h and later kept in a deep freezer with a temperature of  $-20 \pm 2^\circ\text{C}$ . After this operation was repeated 20 times, the resulting color changes were determined by the color measurement device Minolta CR-231 (Anonymous, 2001) with respect to the principles stated in ASTM D2244-07e1 (2007). Figure 1 shows the cross-section of the device mentioned in the standard, which can make measurements according to the  $CIEL^*a^*b^*$  color system.

In the  $CIEL^*a^*b^*$  color system, the differences in colors and their locations are given by the color coordinates  $L^*$ ,  $a^*$ ,  $b^*$ . Here,  $L^*$  is on the black-white ( $L^* = 0$  for black,  $L^* = 100$  for white) axis,  $a^*$  is on

the red-green (positive values are red, negative values are green) axis, and  $b^*$  is on the yellow-blue (positive values are yellow, negative values are blue) axis (Oliver et al., 1992; McGuire, 1992). Figure 2 depicts the  $CIEL^*a^*b^*$  color space.

In order to determine in which color tone the change was effective, the values of red color tone ( $a^*$ ), yellow color tone ( $b^*$ ) and color lightness ( $L^*$ ) were investigated independently, and furthermore, the total color change ( $\Delta E^*$ ) was calculated using the equation:

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

A small value of  $\Delta E^*$  indicates that the color has either not changed

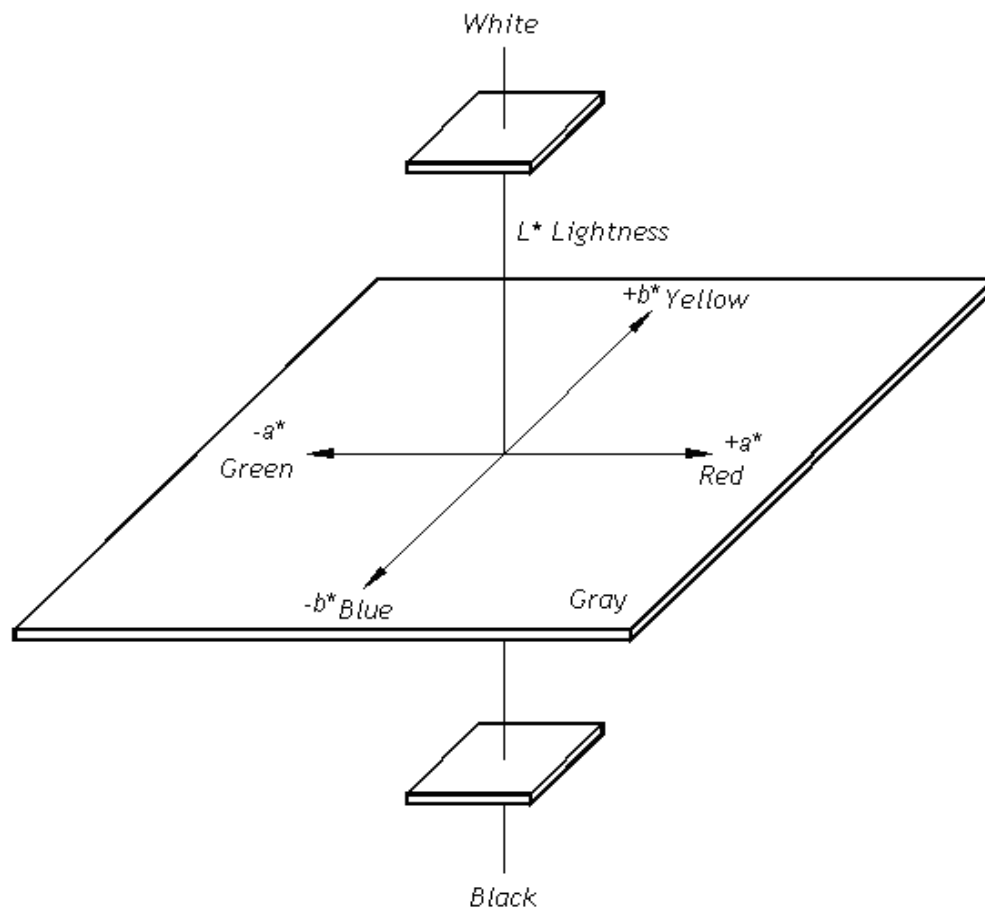


Figure 2. CIEL\*a\*b\* color space.

Table 2. Analysis of variance results for the red color tone.

Source of variation	Degrees of freedom	Sum of squares	Mean square	F Value	Table value $\alpha = 0.05$
Wood Type (A)	2	22.132	11.066	26.1118	0.0000*
Varnish Type (B)	2	58.766	29.383	69.3352	0.0000*
Interaction (AB)	4	5.416	1.354	3.1953	0.0173*
Error	81	34.327	0.424		
Total	89	120.641			

\*Significant at the 0.05 level.

Table 3. Wood-type-wise and varnish-type-wise comparison results.

Wood type	$\bar{x}$	HG	Varnish Type	$\bar{x}$	HG
Pine	4.055	A*	Cellulosic	4.335	A*
Beech	2.916	B	Polyurethane	3.400	B
Oak	3.120	B	Acrylic	2.356	C
LSD $\pm$ 0.3345					

$\bar{x}$  : Arithmetic mean; HG: homogeneity group; \*: indicates an increase in the red color tone.

**Table 4.** Comparison results for the wood type-varnish type interactions.

Varnish type / wood type	Cellulosic		Polyurethane		Acrylic	
	$\bar{x}$	HG	$\bar{x}$	HG	$\bar{x}$	HG
Pine	5.024	A*	3.813	BC	3.328	CD
Beech	4.093	B	3.202	D	1.453	F
Oak	3.887	BC	3.185	D	2.288	E
LSD $\pm$ 0.5794						

$\bar{x}$  : Arithmetic mean; HG: homogeneity group; \*: indicates an increase in the red color tone

**Table 5.** Analysis of variance results for the yellow color tone.

Source of variation	Degrees of freedom	Sum of squares	Mean square	F Value	Table value $\alpha= 0.05$
Wood type (A)	2	13.275	6.638	6.5685	0.0023*
Varnish type (B)	2	199.359	99.679	98.6397	0.0000*
Interaction (AB)	4	13.044	3.261	3.2271	0.0165*
Error	81	81.854	1.011		
Total	89	307.532			

\*: Significant at the 0.05 level.

or changed only by a very small amount.

### Statistical method

The evaluation of the results was made based on the difference of measurements performed before and after the hot and cold-check test. The effects of the factors were assessed by means of the analysis of variance (ANOVA) tests. Whenever the intergroup differences were found to be significant, the Duncan test was used to compare the means. The ranking of the experimental factors was thus determined by clustering the factors into homogeneity groups with respect to the least significant difference (LSD) critical value.

## RESULTS

### Red color tone

Table 2 depicts the analysis of variance results for the red color tone changes on the varnish layers after accelerated aging through the hot and cold-check test. According to these results, the wood type, the varnish type and the pair-wise interactions of these factors were found to be significant ( $\alpha = 0.05$ ). Table 3 exhibits the comparison results of the Duncan test which was later performed among the mean values of the wood types and the varnish types. It can be seen from Table 3 that the highest increase in the red color tone was observed on the pine wood among the wood types and on the cellulosic varnish among the varnish types. The difference between the beech and the oak was insignificant, and the

least increase in the red color tone was observed in the acrylic varnish. Table 4 shows the comparison of results for the wood type-varnish type interactions, obtained by the Duncan test using a critical value of LSD  $\pm$  0.5794. According to these results, the highest increase in the red color tone was observed on the pine wood with cellulosic varnish, whereas the lowest increase was observed on the beech wood with acrylic varnish.

### Yellow color tone

Table 5 demonstrates the analysis of variance results for the yellow color tone on the varnish layers after accelerated aging through the hot and cold-check test. According to these results, the wood type, the varnish type and the pair-wise interactions of these factors were found to be significant ( $\alpha = 0.05$ ). Table 6 shows the comparison of results of the Duncan test which was later performed among the mean values of the wood types and the varnish types.

It can be inferred from the Table 6 that the highest increase in the yellow color tone was observed on the oak wood among the wood types and on the cellulosic varnish among the varnish types. The difference between the pine and the beech was insignificant, and the least increase in the yellow color tone was observed in the acrylic varnish.

Table 7 shows the comparison of results for the wood type-varnish type interactions, obtained by the Duncan

**Table 6.** Wood-type-wise and varnish-type-wise comparison results.

Wood type	$\bar{x}$	HG	Varnish type	$\bar{x}$	HG
Pine	-3.355	B	Cellulosic	-1.096	A*
Beech	-3.536	B	Polyurethane	-3.956	B
Oak	-2.648	A*	Acrylic	-4.484	C
LSD $\pm$ 0.5166					

$\bar{x}$ : Arithmetic mean; HG: homogeneity group; \*: indicates an increase in the yellow color tone.

**Table 7.** Comparison results for the wood type-varnish type interactions.

Varnish type / wood type	Cellulosic		Polyurethane		Acrylic	
	$\bar{x}$	HG	$\bar{x}$	HG	$\bar{x}$	HG
Pine	-0,745	A	-4,439	C	-4,880	C
Beech	-1,336	A	-4,595	C	-4,676	C
Oak	-1,207	A	-2,835	B	-3,895	C
LSD $\pm$ 0.8947						

$\bar{x}$ : Arithmetic mean; HG: homogeneity group; \*: indicates an increase in the yellow color tone.

**Table 8.** Analysis of variance results for the value of color lightness.

Source of variation	Degrees of freedom	Sum of squares	Mean square	F Value	Table value $\alpha= 0.05$
Wood type (A)	2	5.115	2.558	1.1965	0.3075*
Varnish type (B)	2	502.758	251.392	117.6129	0.0000
Interaction (AB)	4	17.415	4.354	2.0369	0.0969*
Error	81	173.134	2.137		
Total	89	698.449			

\*: Insignificant at the 0.05 level.

test using a critical value of LSD  $\pm$  0.8947. According to Table 7, the highest increase in the yellow color tone was observed on the wood samples with cellulosic varnish, whereas the lowest increase was observed on the samples with acrylic varnish.

### Value of color lightness

Table 8 shows the analysis of variance results for the color lightness value changes on the varnish layers after accelerated aging through the hot and cold-check test. According to the analysis of variance results, only the varnish type was found to be significant, while the other factors were insignificant. Table 9 shows the comparison results of the Duncan test which was later performed among the mean values of the varnish types using a

critical value of LSD  $\pm$  0.7510. According to these results, the highest increase was observed on the wood samples with acrylic varnish, while the lowest increase was observed on the samples with cellulosic varnish.

### Total color change

Table 10 exhibits the analysis of variance results for the total color changes on the varnish layers after accelerated aging through the hot and cold-check test. According to the analysis of variance results, the varnish type and the wood type-varnish type interactions were found to be insignificant. Table 11 shows the comparison results of the Duncan test which was later performed. The color changes on various wood types varnished with a range of varnish types have been observed as a result

**Table 9.** Varnish-type-wise comparison results.

Cellulosic		Polyurethane		Acrylic	
$\bar{x}$	HG	$\bar{x}$	HG	$\bar{x}$	HG
-3,439	C	-0,089	B	2,300	A*
LSD $\pm$ 0.7510					

$\bar{x}$  : Arithmetic mean; HG: homogeneity group; \*: indicates an increase in the color lightness value.

**Table 10.** Analysis of variance results for the total color change.

Source of variation	Degrees of freedom	Sum of squares	Mean square	F Value	Table value $\alpha= 0.05$
Wood type (A)	2	24.212	12.106	11.0712	0.0001
Varnish type (B)	2	3.523	1.761	1.6108	0.2061*
Interaction (AB)	4	1.055	0.264	0.2412	ns
Error	81	88.570	1.093		
Total	89	117.359			

\*: Insignificant at the 0.05 level; ns: insignificant.

**Table 11.** Wood-type-wise comparison results.

Pine		Beech		Oak	
$\bar{x}$	HG	$\bar{x}$	HG	$\bar{x}$	HG
6,292	A	5.839	A	5.037	B
LSD $\pm$ 0.5371					

$\bar{x}$  : Arithmetic mean; HG: homogeneity group; \*: indicates the highest increase in the total color change.

of accelerated aging through the hot and cold-check test. Evaluation of the collected data showed that the highest color change was seen on the pine wood with cellulosic varnish. The reason was presumably related to the plastifier in the cellulosic varnish. In the literature, it has been noted that the amount of plastifier in the cellulosic varnish is reduced with increasing temperature, which proportionally causes cracking and yellowing on the surface (Sonmez and Budakci, 2004). Again in the literature, it has been pointed out that when subjected to aging through the hot and cold-check test, the cellulosic varnish is less successful on all surfaces compared to other varnish types (Sonmez and Kesik, 1999; Yolanda, 1998; Sonmez and Ozen, 1996). Observational investigations revealed that none of the samples exhibited visible defects such as cracking, spalling or flaking. This has also been stated the same way in a similar study (Sonmez and Kesik, 1999). However, the polyurethane and acrylic varnishes were observed to be more durable during the tests compared to the cellulosic varnish. The higher durability of these varnishes compared to that of

the cellulosic varnish is denoted in the literature as well (Sonmez and Kesik, 1999; Payne, 1965; Sonmez and Budakci, 2004; Morgans, 1969).

The smallest color change was found in the case of the acrylic varnish. In the literature, this outcome is attributed to the fact that the acrylic varnish resin is of colorless, transparent structure and the layer does not exhibit yellowing as a result of aging in the course of time (Payne, 1965; Sonmez and Budakci, 2004; Morgans, 1969). The wood-type-wise comparisons in the literature signify that the oak wood will experience a relatively larger color change because of the oxidation of the tannin in the wood with atmospheric oxygen (Sonmez and Budakci, 2004; Kollmann, 1984). Nevertheless, the largest color change due to aging through the hot and cold-check test was observed on the pine wood. The reason is assumed to be related to the fact that it comprises resin and etheric oil. In a former study, it has been reported that the ultraviolet (UV) rays cause the color of wood material containing extractive substances like resin to become reddish in a short time and this phenomenon is

observed on woods such as Scots pine and Taurus cedar in a short period of time (Sogutlu and Sonmez, 2006). In this respect, the high color change on the pine wood is in compliance with the literature. Consequently, for the choice of wood type and varnish type to be used in the design of the furniture and decoration elements which are to be exposed to high degrees of temperature change, oak wood with acrylic varnish can be recommended.

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