Effect of Thermal Aging on Colour and Glossiness of UV System Varnish-applied Laminated Parquet Layers

Umit Ayata, Sirri Sahin, Bruno Esteves, and Levent Gurleyen

Changes are reported in perpendicular and parallel glossiness, lightness ($L^*$), red colour ($a^*$) tone, and yellow colour ($b^*$) tone due to thermal aging in beech (Fagus orientalis Lipsky), maple (Acer pseudoplatanus L.), northern red oak (Quercus rubra), American black walnut (Juglans nigra L.), and walnut (Juglans regia L.) wood coated with a UV system commonly used on laminated parquets. Coated samples were exposed to different thermal aging levels (30 °C for 30 days, 60 °C for 60 days, and 90 °C for 90 days). Colour and gloss were determined before and after the thermal aging processes. The $L^*$ decreased for all species with the thermal aging decreasing more for more intense processes. Variations of the $a^*$ and $b^*$ colour parameters depended on the species. The colour parameters changed for temperatures higher than 30 °C. In general, glossiness decreased proportionally to the severity of the thermal aging for all of the species studied.

Keywords: Laminated Parquet; Thermal aging; Colour; Glossiness

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INTRODUCTION

Today there are several production methods for laminate flooring. Most of them are based on the application of a protective layer that is usually a varnish, with or without a primer, to protect the wood material from external environmental effects. In addition to the protection ability of these layers, they also allow a change to the aesthetic of the wood surfaces. With time, these coatings deteriorate due to physical, chemical, and mechanical stresses that change the adhesion of the coating layers and other surface properties (Sonmez et al. 2011). Along with UV degradation, temperature has been reported to have a significant effect on the aging of coatings. Nevertheless, temperature by itself is not enough to break the chemical bonds in most commercial adhesives because the maximum temperature that coatings are subjected to outdoors is around 76 °C, which does not produce enough thermal energy (70 Kcal/mol to 90 Kcal/mol) necessary to cleave the adhesive chemical bonds (Feller 1995; Demirci et al. 2013). In accordance to Holzhausen et al. (2002), earlier thermal aging studies show that evaporation and polymer degradation are the most important processes for the changes in coating properties. Changes depend on thermal exposure temperature and on the length of the exposure time. These authors stated that at lower temperatures the thermal energy is lower than the activation energy for post-linkage or degradation reactions and the aging process is dominated by physical changes, like the evaporation of low molecular coating components. With the increase in exposure temperature, chemical aging processes prevail, resulting in the degradation of the coating.
When subjecting laminate flooring to heat, the changes on the surface are due not only to changes in the coating adhesive, but also in wood. In accordance with Meints et al. (2017), the wood colour ranges between almost white as for example white poplar, passing through various yellowish, reddish and brownish hues to almost black, like ebony. These differences have been attributed to chemical components that interact with light. Shafizadeh and Chin (1977) stated that wood suffers an alteration of chemical composition through a thermal degradation that depends not only on temperature, but also on the exposure time at that temperature.

Although the components of wood generally present a good thermal stability at 100 °C until about 48 h, if they are heated long enough, the chemical bonds of the structural macromolecule begin to break to a significant extent, even for temperatures below 100 °C. The temperature at which the thermal degradation of wood starts depends on the wood species (Kollmann and Fengel 1965) and on the molecular weight and degree of crystallinity of the components (Belville 1982).

In the natural ageing process the changes on wood colour are attributed mainly to photodegradation, which starts with lignin decomposition by UV light (Liu et al. 2017). Nevertheless, temperature is known to accelerate the chemical processes, significantly influencing wood ageing (Tolvaj et al. 2013; Liu et al. 2017). Several works have shown that when the temperature is increased, the lightness ($L^*$) decreases and the decrease is proportional to the temperature and time of exposure (Esteves et al. 2007; Barcik et al. 2015; Ayata et al. 2017b). This decrease is higher in oxidative media, as shown before for Pinus pinaster and Eucalyptus globulus wood (Esteves et al. 2007). In accordance to Chen et al. (2012) the presence of oxygen plays a vital role in the darkening of wood during heat treatment.

In relation to $a^*$ and $b^*$ the changes with temperature depend on the species and on the initial value (Korkut et al. 2013; Ayata et al. 2017a). In some cases, $a^*$ increases with increased temperature as for instance, for Scots pine (Aksoy et al. 2011), larch (Wang et al. 2016) or spruce (Torniainen et al. 2015), and in another cases $a^*$ decreases, as in the case of Pinus nigra (Guller 2014) or wild cherry (Korkut et al. 2013). The increase in $a^*$ and consequently in redness has been attributed to the formation of condensation, degradation and/or oxidation products during heat treatments, mainly due to the condensation of lignin and other related extractives forming products that absorb the complementary light of reddish color (Chen et al. 2012). Similarly, different behaviour for $b^*$ with increasing temperature has been reported for several species. For example, an increase was obtained for wild cherry (Korkut et al. 2013) and a decrease for spruce (Torniainen et al. 2015). The increase in yellowness ($b^*$) was in accordance with Chen et al. (2012) due to hydrolysis reactions in wood resulting in the formation of lower molecular weight yellow phenolic substances, such as flavonoids. Extractives play an important role on the colour changes at higher temperatures and depend on the species (Wei et al. 2017), reinforcing the need to study colour changes for each individual species. Glossiness of the wood surface is known to decrease with increased temperature (Aksoy et al. 2011; Karamanoglu and Akyildiz 2013; Korkut et al. 2013; Gurleyen et al. 2017).

This paper reports the changes in perpendicular and parallel glossiness, lightness ($L^*$), red colour ($a^*$) tone, and yellow colour ($b^*$) tone on thermally aged wood from several species, coated with a UV system commonly used on laminated parquets.

EXPERIMENTAL

Materials
In this study, the wood species selected were beech (*Fagus orientalis* Lipsky), maple (*Acer pseudoplatanus* L.), northern red oak (*Quercus rubra* L.), American black walnut (*Juglans nigra* L.), and walnut (*Juglans regia* L.) wood. Samples with dimensions 60 cm × 10 cm × 2 cm (longitudinal × tangential × radial) were prepared from each untreated wood. Afterwards, samples from each wood were coated with a UV system commonly used for laminated parquet. The application process is described in Table 1. This application was done at the KPS factory (Duzce, Turkey). After the application, the samples were cut into smaller samples of 10 cm × 10 cm × 2 cm. All of the samples were kept in a conditioned room with 65% ± 3% relative humidity and 20 °C ± 2 °C until constant weight was achieved in accordance to the TS 2471 (1976) standard.

Table 1. Laminated Parquet Flooring Production Process

<table>
<thead>
<tr>
<th>Polishing production line speed of 10 m/min</th>
<th>Sanding and Calibrating Machines (80 to 120 to 220 grit sizes)</th>
<th>Roller UV parquet paste (white - 25 g/m²)</th>
<th>UV lamp drying (80 °C)</th>
<th>Amount of Kneho-lacke GmbH, UV Sealer Clear S to be applied (25 g/m²) part 1</th>
<th>UV lamp drying (80 °C)</th>
<th>Amount of Kneho-lacke GmbH, UV Sealer Clear S to be applied (25 g/m²) part 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polishing production line speed of 10 m/min</td>
<td>UV lamp drying (400 °C)</td>
<td>280 to 320 grip sandpaper</td>
<td>Amount of Kneho-lacke GmbH, UV Antiscratch Semi Matt W to be applied (7.5 g/m²) part 1</td>
<td>UV lamp drying (80 °C)</td>
<td>Amount of Kneho-lacke GmbH, UV Antiscratch Semi Matt W to be applied (7.5 g/m²) part 2</td>
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Thermal aging process
The thermal aging was conducted in a Mikrotest MST Series oven (Mikrotest, Ankara, Turkey) with different aging temperatures and duration in accordance to Table 2. One control sample was kept with no aging to compare colour and glossiness with the aged samples.

Table 2. Thermal Aging Process by Using an Oven

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Control (unaged)</td>
<td>30 °C for 30 days</td>
<td>60 °C for 60 days</td>
<td>90 °C for 90 days</td>
<td></td>
</tr>
</tbody>
</table>

Methods

Colour measurement
The colour change of the control and thermally aged samples coated with a common UV system used in laminated materials (Table 1) was determined using an X Rite Ci62 Series Portable Spectrophotometer (X Rite) made in Regensdor, Switzerland (Wavelength Resolution 10 nm, Measurement Geometry D/8°) with a D65 standard illuminant (Fig. 1). The CIELAB system is characterized by three parameters, *L**, *a**, and *b**. The *L** axis represents the lightness, +*a* is the red, -*a* for green, +*b* for yellow, -*b* for blue, and *L* varies from 100 (white) to zero (black) (Zhang *et al.* 2009). The corresponding variations Δ*L*, Δ*a*, and Δ*b*, with the thermal aging process, were calculated using the unaged control as a reference. The total colour difference (ΔE*) was calculated by using Eq. 1,

\[ \Delta E^* = \left[ (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right]^{1/2} \] (1)
where $\Delta L^*$ is the difference $L^{*\text{aged}} - L^{*\text{unaged}}$, $\Delta a^*$ is $a^{*\text{aged}} - a^{*\text{unaged}}$, and $\Delta b^*$ is $b^{*\text{aged}} - b^{*\text{unaged}}$.

**Glossiness measurement**

Surface brightness measurements in perpendicular and parallel directions were made for all samples, thermally aged and unaged, according to ISO 2813 (1994) with a Gloss Meter Poly-gloss GL0030 TQC device (TQC BV, Neuss, Germany), as shown in Fig. 1. The first gloss measurements at 60° angle showed that the correct angle measurement in accordance to ISO 2813 was 85°, so this angle was chosen for the measurements.

**Statistical analysis**

The perpendicular and parallel glossiness at 85°, red colour ($a^*$) tone, lightness ($L^*$), and yellow colour ($b^*$) tone values were measured using ten replicates of each sample and an average value was reported for all materials. The SPSS 17 Software programme (Sun Microsystems, Inc., Santa Clara, CA, USA.) was used for determining the statistical analysis.

**RESULTS AND DISCUSSION**

The initial colour parameters from all of the tested species were different, as was shown by the variance analysis (Table 3). Lightness was higher for maple (75) followed by beech (69), oak (60), walnut (59), and American black walnut (50). The surface of walnut was more red than the other species, which was indicated by the higher $a^*$ ($a^* = 11.81$), while maple had the lowest red content ($a^* = 6.24$). In contrast, beech had the highest yellow content ($b^* = 23.89$), and American black walnut had the lowest ($b^* = 17.78$). Lightness ($L^*$) decreased for all species and processes and the decrease was higher for more severe thermal aging, as shown in Fig. 2. Even at 30 °C, lightness decreased for all of aged samples proving that chemical changes can occur at temperatures lower than 100°C if heated for a long time. The variance analysis showed that the differences in $L^*$ were significant at a 95% confidence level. The highest decrease was observed for maple and the lowest for American black walnut, which was probably due to the initial lightness of these samples. The decrease in lightness at increased temperature was reported earlier for *Pinus radiata* sapwood boards during drying at various schedules starting at 50 °C (McCurdy et al. 2005).
Fig. 2. Initial $L^*$, $a^*$, $b^*$, and $\Delta E^*$ after different thermal aging processes for the studied species.

Table 3. SPSS Analysis Results for Colour Parameters and Glossiness of the Studied Species

<table>
<thead>
<tr>
<th>Test Aging</th>
<th>N</th>
<th>Maple</th>
<th>A. Black Walnut</th>
<th>Walnut</th>
<th>Beech</th>
<th>N. Red Oak</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mean HG</td>
<td>Mean HG</td>
<td>Mean HG</td>
<td>Mean HG</td>
<td>Mean HG</td>
</tr>
<tr>
<td>A</td>
<td>10</td>
<td>75.38 (0.18)</td>
<td>A*</td>
<td>49.71 (0.42)</td>
<td>P</td>
<td>59.18 (0.10)</td>
</tr>
<tr>
<td>B</td>
<td>10</td>
<td>74.73 (0.20)</td>
<td>B</td>
<td>48.44 (0.16)</td>
<td>R</td>
<td>57.65 (0.39)</td>
</tr>
<tr>
<td>C</td>
<td>10</td>
<td>73.25 (0.16)</td>
<td>C</td>
<td>47.19 (0.16)</td>
<td>S</td>
<td>55.75 (0.26)</td>
</tr>
<tr>
<td>D</td>
<td>10</td>
<td>68.23 (0.86)</td>
<td>E</td>
<td>46.34 (0.25)</td>
<td>T</td>
<td>54.87 (0.12)</td>
</tr>
</tbody>
</table>

Values in parentheses are standard deviations, HG: Homogeneous Group, N: Number of measurements, Mean: Average, *: Maximum value, A: Control, B: 30°C for 30 days, C: 60°C for 60 days, D: 90°C for 90 days

In the last few years several authors reported this decrease for higher temperatures (Aksoy et al. 2011; Korkut et al. 2013; Barcik et al. 2015) which has been attributed before to coloured degradation products from hemicelluloses and extractives (Sundqvist and
Morén 2002; Sehlstedt-Persson 2003) or lignin. In relation to \( a^* \) and \( b^* \), the variation is dependent on the species, as previously reported, for heat-treated wood (Bekhta and Niemz 2003; Aksoy et al. 2011). For maple, American black walnut, and walnut \( a^* \) decreased for the first two thermal aging processes and increased for the third. In contrast, for beech wood there was an increase followed by a decrease, and for northern red oak all of the samples showed an increase in relation to the control sample, but with no consistent variation according to the severity of the aging process (Fig. 2). The variation in \( b^* \) was inconsistent for the studied species, increasing or decreasing for different thermal aging processes. Nevertheless, for the thermal aging at 90 °C for 90 days, the final \( b^* \) was higher than the control’s for all of the species studied (Fig. 2). The variance analysis showed that the differences in \( a^* \) and \( b^* \) were not significant at a 95% confidence level. Results showed that colour parameters changed with thermal aging, even at temperatures as low as 30 °C, considering they were exposed for periods long enough. The initial gloss measurements at 60° angle showed gloss ranges between 10.48 and 14.74 for perpendicular glossiness and from 14.30 to 20.19, which means that the samples can be considered to have near matt surfaces in accordance to ISO 2813. Therefore the correct angle for gloss measurements is 85°. Glossiness parallel to the fibres direction was much higher than in the perpendicular direction for unaged and aged samples. The differences along the aging process were only significantly different at 95% confidence level for maple (Table 3). Nevertheless, in general, glossiness decreased for all of the species studied, and this decrease was proportional to the severity of the thermal aging. Even at 30 °C, there was a decrease in glossiness of the surface. The highest differences were observed for northern red oak, while the smallest differences were observed for American black walnut. These results reinforced the hypothesis that thermal aging was different for each species. Earlier findings have shown that temperature and time have a significant effect on glossiness (Aksoy et al. 2011; Demirci et al. 2013). The total colour difference (\( \Delta E^* \)) increased for all thermal aging processes and the increase was higher for more severe aging. Major differences were observed for maple, and smaller differences for American black walnut, as shown in Fig. 2. This work can bring some enlighten on the contribution of temperature in colour changes suffered by aging of the studied species.

CONCLUSIONS

With thermal aging, \( L^* \) decreased for all species, and the decrease was higher for more severe thermal aging processes while, for \( a^* \) and \( b^* \), the variation was dependent on the species and on the conditions of the aging process. Results showed that colour parameters changed with thermal aging even at temperatures as low as 30 °C, under the assumption that they were exposed for long periods of time. Generally, glossiness decreased for all of the species studied and this decrease was proportional to the severity of the thermal aging.

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