

## Effect of Thermal Ageing on the Gloss and the Adhesion Strength of the Wood Varnish Layers

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The present study investigated the effect of thermal ageing of several wood varnishes on film characteristics. For this purpose, alkyd, two-part polyurethane (urethane-alkyd), and water-borne (self-cross-linked polyurethane) varnishes were applied on Scots pine (*Pinus sylvestris* L.), Eastern beech (*Fagus orientalis* L.), and sessile oak (*Quercus petraea* L.). The test samples had 8% or 12% moisture content. The samples were then thermally aged for 25, 50, 75, and 100 days at 25, 50, 75, and 100°C. The decrease in adhesion strength of the varnish layers and the loss in surface gloss were determined in accordance with the ISO 4624 and ISO 2813 standards. The results of the study indicated that thermal ageing caused a decrease in the adhesion strength and gloss values.

*Key Words:* Woodmaterials; Moisture content; Wood varnishes; Thermal ageing; Adhesion strength; Gloss.

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### INTRODUCTION

The physical, chemical, and mechanical effects that the protective layer (paint/varnish) on wooden material encounters cause the cohesive and the adhesive strength to weaken in time, lowering the performance of the material (Sönmez 2005). Ultraviolet radiation was reported to promote the ageing of several polymeric materials (plastic and wood materials), and temperature was reported as a significant parameter in ageing (Andrady *et al.* 1998). However, the effect of temperature is not sufficient to break the chemical bonds within commercial polymers. Energy of 70 to 90 kcal/mol is required to break these bonds. Additionally, it was reported that the presence of moisture in the environment enhanced the effect of temperature (Feller 1994).

In addition, physical and chemical ageing causes internal tension in the structure of organic varnishes and paints. The cracking resistance of the top layer is considerable within 25 °C to 60 °C, but above 80 °C the wood starts to get rigid. While the brightness crossing point has been shown as a function of applied temperature and time, it is more important that temperature and time are applied to characteristics of the varnish in long-term protection (Holzhausen *et al.* 2002; Sönmez *et al.* 2011a).

When layers of varnish or paint are exposed to various moisture and temperature conditions in a UV test, UV-degradation may be added on top of damage caused by temperature and humidity. As a result of this, micro-cracking occurs (Ochs and Vogelsang 2004). In a different study, a polyurethane topcoat system was exposed to UV ageing and it was reported that high temperature played an important role in the degradation of varnish molecules on the surface. Bubble formation was observed, resulting in an increase in surface roughness and a decrease in surface brightness (Yang *et al.* 2002).

While UV radiation carried by the rays of the sun drives photo-oxidation, the sun also creates high temperature, thermal ageing, and hydrolysis. Resistant polymer bonds are also broken as a result of photo-oxidation (Oosterbroek *et al.* 1991; Perera and Oosterbroek 1994; Perera 1995, 1998, 2001).

Despite the increasing number of studies on the topic, the ageing treatment processes affecting the characteristics of the protective layer are still complicated, debatable, and the consequences are not yet satisfactorily explained. With these concerns in mind, the aim of the conducted study is to determine the effect of thermal ageing of wood varnish on the gloss and the adhesion strength of varnish layers.

## EXPERIMENTAL

### Materials

#### *Wood material*

Wood samples of Scots pine (*Pinus sylvestris* L.), Eastern beech (*Fagus orientalis* L.), and oak (*Quercus petraea* L.) were used during experimental preparation due to their common use in the furniture and decoration industry in Turkey. The samples were prepared from the sapwood parts of randomly selected first-grade timbers; the following characteristics were chosen: regular-fiber, knotless, crack-free, exhibiting no variation in color or density, and having annual rings perpendicular to the surface, with regard to the principles in ISO 3129 (2012).

Samples with a moisture content ensured by air-drying were cut into the dimensions of 110 x 110 x 12 mm as roughcast. Then, the samples were left in air-conditioning cabinets; at  $20 \pm 2$  °C temperature and  $42 \pm 5\%$  relative humidity for 8% moisture content, and at  $20 \pm 2$  °C temperature and  $65 \pm 5\%$  relative humidity for 12% moisture content until their mass no longer varied (ISO 3130 1975). The samples were then dimensioned to 100 x 100 x 10 mm and sanded with 80-grit (on Norton scale) sandpaper and then with 100-grit sandpaper for varnishing. According to the experimental design, a total of 1440 pieces were prepared by creating four samples in order to obtain data for each factor: three wood types, two moisture contents, three varnish types, four thermal processing temperatures, and five thermal processing durations.

#### *Varnishes*

Alkyd, two-part polyurethane (urethane-alkyd), and water-borne (self-cross-linked polyurethane) varnishes were used to varnish the test samples. Alkyd and two-part polyurethane are reactive finishes. They are composed of small molecules that resemble the blocks in a set of Tinker Toys. In a can of finish, these molecules are floating in a thinner. As the thinner evaporates, the molecules approach each other and connect either with the help of oxygen (alkyd varnish) or with the aid of a catalyst, activator, cross-linker, or hardener (two-part polyurethane). Water-borne varnishes are the only coalescing finishes. They are composed of droplets (latexes) resembling microscopic soccer balls with plastic covers and solid insides. The insides are a reactive finish that has been cross-linked. The droplets are suspended in water and a very slowly evaporating solvent. The water evaporates first. The solvent then softens the outside of droplets (as solvent would soften the outer skin on plastic soccer balls). The droplets become sticky and stick together when solvent evaporates (Flexner 2005). The application conditions of

varnishes were prepared according to the manufacturer's suggestions and in accordance with the standard ASTM D 3023-98 (2011). Technical specifications of the varnishes and application systems used are given in Table 1.

**Table 1.** Technical Specifications of Varnishes and Application Systems Used

| Varnish Type                          | pH   | Density (g/cm <sup>3</sup> ) | Application viscosity (sn DIN Cup/4mm) | Amount of finish application (g/m <sup>2</sup> ) | Solid content (%) | Conventional spray gun tip diameter (mm) | Air pressure (Bar) |
|---------------------------------------|------|------------------------------|--|--|-------------------|--|--------------------|
| Two-part polyurethane (Filling)       | 5.94 | 0.98                         | 18                                     | 125  | 48.1              | 1.8                                      | 2                  |
| Two-part polyurethane (Topcoat-Gloss) | 4.01 | 0.99                         | 18                                     | 125  | 44.2              | 1.8                                      | 2                  |
| Alkyd (Gloss)                         | 5.51 | 0.94                         | 18                                     | 100  | 53.2              | brush                                    | brush              |
| Water-borne (Primer)                  | 9.17 | 1.014                        | 18                                     | 100  | 14.20             | 1.3                                      | 1                  |
| Water-borne (Filling)                 | 9.30 | 1.015                        | 18                                     | 67   | 34.13             | 1.3                                      | 1                  |
| Water-borne (Topcoat-Gloss)           | 8.71 | 1.031                        | 18                                     | 67   | 31.83             | 1.3                                      | 1                  |

Alkyd varnish was applied with a brush as two coats filling and two coats topcoat. Firstly, two-part polyurethane and water-borne filling varnishes were applied on the sample surfaces; then, the same type of two coats topcoat varnishes were applied on those at room temperature (~ 20 °C) with a conventional spray gun. The amount of varnish applied was determined by weighing with a sensitive analytical scale of ± 0.01 g. The samples were then dried at 20 °C and at a relative humidity of 65 ± 5% under laboratory conditions and kept until they reached a constant weight (ASTM D 3023-98 2011; Budakçı and Sönmez 2010).

## Methods

### *Thermal ageing*

Varnished experimental samples were exposed to thermal ageing at 25, 50, 75, and 100 °C temperatures in dry air sterilizers (ovens) for a period of 25, 50, 75, and 100 days, respectively, and kept in the air-conditioned cabinet until reaching an 8% to 12% equilibrium moisture content.

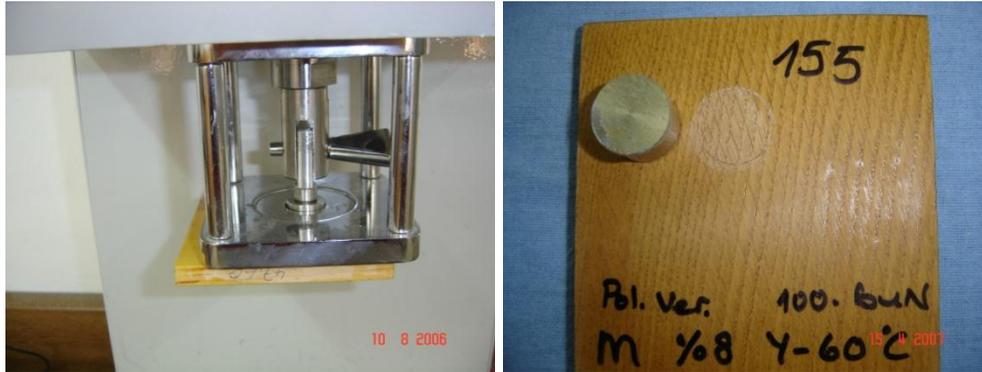
### *Adhesion Strength (Pull - Off) Test*

The adhesion strength of the varnish layers was determined using the adhesion test machine displayed in Fig. 1 as instructed by the ISO 4624 principles (Budakçı 2006; Budakçı and Sönmez 2011). The steel test cylinders with Ø 20 mm were attached to the sample surfaces at room temperature (~ 20 °C) via the help of a cast system. A highly adhesive binding agent that has no solvent effect on the two-part epoxy resin protective layers was used during the tests as indicated in the ISO 4624 standard at a measure of 150 ± 10 g/m<sup>2</sup>.

The adhesion strength ( $X$ ) was calculated (MPa) according to the following equation (ISO 4624 2002),

$$X = 4F / \pi.d^2 \quad (1)$$

where  $F$  is the force at the moment of failure (in Newton) and  $d$  is the diameter of the test cylinder (in mm).



**Fig. 1.** Adhesion test machine and test sample

### *Gloss Test*

The variation in the gloss of the varnish layers was determined using a glossmeter, which takes measurements at  $60^\circ$ , as displayed in Fig. 2. The set-up is specified in ISO 2813 (1994). The ratio with which the light shining on a surface reflects is measured in determining the gloss of the paint and varnish layers. Generally speaking, a  $20^\circ$  angle is used to measure the surface gloss of matte layers, a  $60^\circ$  angle is used for both matte and glossy layers, and an  $85^\circ$  angle is used for very glossy and shiny layers in tests measurements (Sönmez 1989).

The test equipment was recalibrated prior to each measurement and in between measurements using black glass with a gloss number 100 for each geometry and with a smooth surface refraction index of 1.567.



**Fig. 2.** Glossmeter and principle of measurement

### *Statistical evaluation*

In the evaluation of data, the statistical package software MSTATC was used. In the analysis, the values of factors were determined as a result of multiple variance analysis. Factor effects were considered significant with  $\alpha = 0.05$  error probability. According to variance analysis “ANOVA” results, Least Significant Difference (LSD) critical values were used and causing factors were determined.

## RESULTS AND DISCUSSION

### Adhesion Strength

The arithmetic average of the measured adhesion strength values of the samples were determined to be different with respect to the moisture content, type of varnish, thermal processing temperature, and thermal processing time. Multivariate ANOVA analysis was carried out in order to determine the factor(s) that caused the difference in reference to the type of wood sample.

#### *Scots pine*

The results of the analysis of variance for the Scots pine samples are displayed in Table 2.

**Table 2.** Results of Variance Analysis of Scots Pine Samples

| Source of Variance | Degrees of freedom | Sum of squares | Mean square | F-value  | Prob. $\alpha=0.05$ |
|--------------------|--------------------|----------------|-------------|----------|---------------------|
| Factor A           | 1                  | 3.067          | 3.067       | 9.9202   | 0.0018              |
| Factor B           | 2                  | 71.160         | 35.580      | 115.0762 | 0,0000              |
| Interaction AB     | 2                  | 1.870          | 0.935       | 3.0245   | 0.0498*             |
| Factor C           | 3                  | 0.969          | 3.323       | 1.0445   | 0.3729*             |
| Interaction AC     | 3                  | 2.013          | 0.671       | 2.1700   | 0.0912*             |
| Interaction BC     | 6                  | 3.270          | 0.620       | 2.0053   | 0.0642*             |
| Interaction ABC    | 6                  | 4.491          | 0.749       | 2.4211   | 0.0263              |
| Factor D           | 4                  | 30.472         | 7.618       | 24.6389  | 0.0000              |
| Interaction AD     | 4                  | 6.976          | 1.744       | 5.6406   | 0.0002              |
| Interaction BD     | 8                  | 8.147          | 1.018       | 3.2935   | 0.0012              |
| Interaction ABD    | 8                  | 5.969          | 0.746       | 2.4132   | 0.0151              |
| Interaction CD     | 12                 | 2.097          | 0.175       | 0.5652   | ns                  |
| Interaction ACD    | 12                 | 10.430         | 0.868       | 2.8112   | 0.0011              |
| Interaction BCD    | 24                 | 24.323         | 1.013       | 3.2778   | 0.0000              |
| Interaction ABCD   | 24                 | 34.432         | 1.435       | 4.6400   | 0.0000              |
| Error              | 360                | 111.308        | 0.309       |          |                     |
| Total              | 479                | 321.445        |             |          |                     |

Factor A: Moisture content, B: Varnish type, C: Thermal processing temperature, D: Thermal processing time, \*: Meaningless; ns: insignificant (according to  $\alpha=0.05$ )

The results displayed in Table 2 indicate that factor C and factor interactions AB, AC, and BC were meaningless, whereas the factor interaction CD was insignificant at a significance level of  $\alpha=0.05$ . The comparison results of the Duncan test on the factor levels A, B, and D that was conducted using the LSD critical value are displayed in Table 3. The adhesion strength of the samples with 8% moisture content was determined to be higher, as shown in Table 3. The adhesion strength was the highest for alkyd varnish and the lowest for the water-borne varnish.

The comparison of the thermal processing time indicated that the adhesion strength of the test samples aged for 75 and 100 days were similar and that the control samples delivered the highest adhesion strength.

**Table 3.** Comparison Results of Duncan Test of Scots Pine Samples (MPa)

|                                |           |    |
|--------------------------------|-----------|----|
| Moisture content               | $\bar{x}$ | HG |
| 8%                             | 3.661     | A* |
| 12%                            | 3.501     | B  |
| LSD $\pm$ 0.09971              |           |    |
| Varnish type                   | $\bar{x}$ | HG |
| Alkyd                          | 4.021     | A* |
| Two-part polyurethane          | 3.637     | B  |
| Water-borne                    | 3.083     | C  |
| LSD $\pm$ 0.1221               |           |    |
| Thermal processing time (Days) | $\bar{x}$ | HG |
| Control                        | 4.066     | A* |
| 25                             | 3.572     | B  |
| 50                             | 3.482     | BC |
| 75                             | 3.374     | C  |
| 100                            | 3.409     | C  |
| LSD $\pm$ 0.1577               |           |    |

$\bar{x}$  : Average value HG: The homogeneous group \* : The highest adhesion strength value.

#### *Eastern beech*

The results of the analysis of variance for the Eastern beech samples are displayed in Table 4.

**Table 4.** Results of Variance Analysis of Eastern Beech Samples (MPa)

| Source of Variance | Degrees of freedom | Sum of squares | Mean square | F-value | Prob. $\alpha=0.05$ |
|--------------------|--------------------|----------------|-------------|---------|---------------------|
| Factor A           | 1                  | 0.238          | 0.238       | 0.3821  | ns                  |
| Factor B           | 2                  | 120.167        | 60.083      | 96.4324 | 0.0000              |
| Interaction AB     | 2                  | 7.851          | 3.926       | 6.3005  | 0.0020              |
| Factor C           | 3                  | 3.592          | 1.197       | 1.9214  | 0.1257*             |
| Interaction AC     | 3                  | 3.143          | 1.048       | 1.6813  | 0.1706*             |
| Interaction BC     | 6                  | 7.282          | 1.214       | 1.9478  | 0.0724*             |
| Interaction ABC    | 6                  | 12.412         | 2.069       | 3.3200  | 0.0034              |
| Factor D           | 4                  | 35.199         | 8.800       | 14.1234 | 0.0000              |
| Interaction AD     | 4                  | 2.712          | 0.678       | 1.0882  | 0.3621*             |
| Interaction BD     | 8                  | 49.586         | 6.198       | 9.9480  | 0.0000              |
| Interaction ABD    | 8                  | 5.249          | 0.656       | 1.0531  | 0.3957*             |
| Interaction CD     | 12                 | 17.158         | 1.430       | 2.2949  | 0.0080              |
| Interaction ACD    | 12                 | 15.695         | 1.308       | 2.0992  | 0.0164              |
| Interaction BCD    | 24                 | 70.038         | 2.918       | 4.6837  | 0.0000              |
| Interaction ABCD   | 24                 | 20.026         | 0.834       | 1.3392  | 0.1342*             |
| Error              | 360                | 224.302        | 0.623       |         |                     |
| Total              | 479                | 594.649        |             |         |                     |

Factor A: Moisture content, B: Varnish type, C: Thermal processing temperature, D: Thermal processing time, \*: Meaningless; ns: insignificant (according to  $\alpha= 0.05$ )

The results displayed in Table 4 indicated that factor C and factor interactions AC, BC, AD, ABD, and ABCD were meaningless, whereas factor A was insignificant at  $\alpha = 0.05$ . The comparison results of the Duncan test on the factor levels B and D that were conducted using the LSD critical value are displayed in Table 5.

**Table 5.** Comparison Results of Duncan Test of Eastern Beech Samples (MPa)

|                                |           |    |
|--------------------------------|-----------|----|
| Varnish type                   | $\bar{x}$ | HG |
| Alkyd                          | 4.897     | A* |
| Two-part polyurethane          | 4.391     | B  |
| Water-borne                    | 3.677     | C  |
| LSD $\pm$ 0.1734               |           |    |
| Thermal processing time (Days) | $\bar{x}$ | HG |
| Control                        | 4.585     | AB |
| 25                             | 4.619     | A* |
| 50                             | 3.908     | C  |
| 75                             | 4.365     | B  |
| 100                            | 4.131     | C  |
| LSD $\pm$ 0.2239               |           |    |

$\bar{x}$  : Average value HG: The homogeneous group \*: The highest adhesion strength value.

The adhesion strength was the highest for alkyd varnish and the lowest for the water-borne varnish. The comparison of the thermal processing time indicated that the adhesion strength of samples aged for 25 days was high while adhesion strength of test samples aged for 50 and 100 days was low.

#### *Sessile oak*

The results of the analysis of variance for the sessile oak samples are displayed in Table 6.

**Table 6.** Results of Variance Analysis of Sessile Oak Samples

| Source of Variance | Degrees of freedom | Sum of squares | Mean square | F-value  | Prob. $\alpha=0.05$ |
|--------------------|--------------------|----------------|-------------|----------|---------------------|
| Factor A           | 1                  | 0.215          | 0.215       | 0.5387   | ns                  |
| Factor B           | 2                  | 217.472        | 108.736     | 272.4043 | 0.0000              |
| Interaction AB     | 2                  | 14.990         | 7.495       | 18.7763  | 0.0000              |
| Factor C           | 3                  | 3.519          | 1.173       | 2.9387   | 0.0332              |
| Interaction AC     | 3                  | 2.363          | 0.788       | 1.9735   | 0.1176*             |
| Interaction BC     | 6                  | 5.293          | 0.882       | 2.2100   | 0.0416              |
| Interaction ABC    | 6                  | 2.162          | 0.360       | 0.9027   | ns                  |
| Factor D           | 4                  | 18.685         | 4.671       | 11.7022  | 0.0000              |
| Interaction AD     | 4                  | 2.900          | 0.725       | 1.8160   | 0.1251*             |
| Interaction BD     | 8                  | 45.607         | 5.701       | 14.2816  | 0.0000              |
| Interaction ABD    | 8                  | 4.222          | 0.528       | 1.3222   | 0.2309*             |
| Interaction CD     | 12                 | 20.293         | 1.691       | 4.2364   | 0.0000              |
| Interaction ACD    | 12                 | 8.310          | 0.693       | 1.7349   | 0.0579*             |
| Interaction BCD    | 24                 | 55.869         | 2.328       | 5.8318   | 0.0000              |
| Interaction ABCD   | 24                 | 17.613         | 0.734       | 1.8385   | 0.0103              |
| Error              | 360                | 143.702        | 0.399       |          |                     |
| Total              | 479                | 563.215        |             |          |                     |

Factor A: Moisture content, B: Varnish type, C: Thermal processing temperature, D: Thermal processing time, \*: Meaningless; ns: insignificant (according to  $\alpha=0.05$ )

The results displayed in Table 6 indicated that the factor interactions AC, AD, ABC, and ACD were meaningless, whereas factor A and factor interaction ABC were insignificant at a significance level of  $\alpha=0.05$ . The comparison results of the Duncan test on the factor levels B, C, and D that was conducted using the LSD critical value are displayed in Table 7.

**Table 7.** Comparison Results of Duncan Test of Sessile Oak Samples (MPa)

| Varnish type                                   | $\bar{x}$ | HG |
|--|-----------|----|
| Alkyd  | 4.786     | A* |
| Two-part polyurethane                          | 4.461     | B  |
| Water-borne                                    | 3.224     | C  |
| LSD $\pm$ 0.9500                               |           |    |
| Thermal processing temperature ( $^{\circ}$ C) | $\bar{x}$ | HG |
| 25   | 4.266     | A* |
| 50   | 4.057     | B  |
| 75   | 4.092     | B  |
| 100  | 4.214     | AB |
| LSD $\pm$ 1.097                                |           |    |
| Thermal processing time (Days)                 | $\bar{x}$ | HG |
| Control  | 4.460     | A* |
| 25   | 4.306     | A* |
| 50   | 3.980     | B  |
| 75   | 4.095     | B  |
| 100  | 3.944     | B  |
| LSD $\pm$ 1.227                                |           |    |

$\bar{x}$  : Average value HG: The homogeneous group \*: The highest adhesion strength value.

The adhesion strength was the highest for alkyd varnish and the lowest for the water-borne varnish, as shown in the Table 7. The adhesion strength of the samples that were aged at 25  $^{\circ}$ C was determined to be the highest at the level of thermal processing temperature. The comparison of the thermal processing time indicated that the adhesion strength of the test samples aged for 50, 75, and 100 days were similar and low whereas those of the control and the samples aged for 25 days were the highest.

The results of the study indicated that moisture content was an insignificant factor in evaluating the adhesion strength of the thermally aged samples. On the other hand, the adhesion strength was observed to decrease with increasing thermal processing temperature and time in all samples that were tested. The highest adhesion strength was observed in the Eastern beech samples. This might have stemmed from the small vessel size and homogeneous structure of the material resulting in the formation of a smoother surface, creating a stronger specific adhesion. It was reported in the literature that the adhesion strength of coniferous tree materials is lower than other species. In the present study, Scots pine samples have the lowest adhesion strength in accordance with the available literature (Nelson 1995; Sönmez and Budakçı 2004; Budakçı and Sönmez 2010).

Comparison of sessile oak and Eastern beech indicated that the sessile oak samples had lower adhesion strength than the beech samples. Sessile oak has a rough surface owing to its rings, large vessels, and a heterogeneous structure. Surface roughness

is one of the most significant factors affecting surface adhesion performance. Because of its structure, the varnish liquid could not penetrate through the vessel voids in the oak samples, leaving air cavities invisible to the naked eye, thus lacking in establishing the necessary mechanical adhesion (Budakçı and Sönmez 2010).

In general, the adhesion strength of the water-borne varnishes was observed to be lower than that of the solvent-based varnishes. This observation was in accordance with the available literature (Sönmez *et al.* 2004). Varnish types that dry via going through a chemical reaction on the wood surface such as acrylic or polyurethane varnish were reported in the literature to have high adhesion strength. This situation was explained by the fact that the alkyd resin that was used in the manufacture of the varnish forms a chemical bond with the cellulose in the wood material (Payne 1965; Jaic and Zivanovic 1997; Sönmez 2005; Budakçı and Sönmez 2010). However, lower adhesion strength was observed for the two-part polyurethane varnish in comparison to the alkyd varnish in the present study. This result was thought to stem from the fact that the variations in temperature and moisture content during treatment caused stress in-between the varnish layers. Since the stress would be more apparent in two-part polyurethane varnish layers possessing larger polymeric molecules, it would have caused a decrease in adhesion resulting in lowered adhesion strength. The high adhesion strength observed in the test samples with alkyd varnish application was thought to stem from the thermoplastic structure of the alkyd varnish and its lipid compound content. The flexible structure of the lipid compounds would have reduced the stress that forms during thermal ageing, thus causing higher adhesion strength values to be measured.

The adhesion strength of the control samples and the measurements taken on day 25 were high in the study. As the thermal processing time increased, a decrease in the adhesion strength was observed. The reduction in the adhesion strength of the clear varnish layers as a result of thermal effects is a significant indicator of the fact that these layers were not sufficient to protect the wooden material surfaces against these thermal effects.

## Gloss

The arithmetic average of the measured gloss values of the samples was determined to depend on the moisture content, type of varnish, thermal processing temperature, and thermal processing time. Multivariate ANOVA analysis was carried out in order to determine the factor(s) that caused the difference in reference to the type of wood sample.

## Scots pine

The results of the analysis of variance for the Scots pine samples are displayed in Table 8. These results indicate that the factors and the factor interactions were meaningful at a significance level of  $\alpha = 0.05$ . The comparison results of the Duncan test on the factor levels of moisture content, type of varnish, thermal processing temperature, and thermal processing time, which was conducted using the LSD critical value, are displayed in Table 9.

**Table 8.** Results of Variance Analysis of Scots Pine Samples

| Source of Variance | Degrees of freedom | Sum of squares | Mean square | F-value   | Prob. $\alpha=0.05$ |
|--------------------|--------------------|----------------|-------------|-----------|---------------------|
| Factor A           | 1                  | 556.852        | 556.852     | 36.5586   | 0.0000*             |
| Factor B           | 2                  | 304605.994     | 152302.997  | 9999.0383 | 0.0000              |
| Interaction AB     | 2                  | 5415.502       | 2707.751    | 177.7700  | 0.0000              |
| Factor C           | 3                  | 306.747        | 102.249     | 6.7129    | 0.0002              |
| Interaction AC     | 3                  | 183.869        | 61.290      | 4.0238    | 0.0078              |
| Interaction BC     | 6                  | 216.724        | 36.121      | 2.3714    | 0.0293              |
| Interaction ABC    | 6                  | 568.503        | 94.751      | 6.2206    | 0.0000              |
| Factor D           | 4                  | 459.732        | 114.933     | 7.5456    | 0.0000              |
| Interaction AD     | 4                  | 272.101        | 68.025      | 4.4660    | 0.0016              |
| Interaction BD     | 8                  | 382.365        | 47.796      | 3.1379    | 0.0019              |
| Interaction ABD    | 8                  | 347.750        | 43.469      | 2.8538    | 0.0044              |
| Interaction CD     | 12                 | 1062.874       | 88.573      | 5.8150    | 0.0000              |
| Interaction ACD    | 12                 | 1397.267       | 116.439     | 7.6445    | 0.0000              |
| Interaction BCD    | 24                 | 3055.231       | 127.301     | 8.3576    | 0.0000              |
| Interaction ABCD   | 24                 | 2815.264       | 117.303     | 7.7012    | 0.0000              |
| Error              | 360                | 5483.435       | 15.232      |           |                     |
| Total              | 479                | 327130.212     |             |           |                     |

Factor A: Moisture content, B: Varnish type, C: Thermal processing temperature, D: Thermal processing time \*: Meaningful (according to  $\alpha=0.05$ )

**Table 9.** Comparison Results of Duncan Test of Scots Pine Samples

|  |           |    |
|--|-----------|----|
| Moisture content                               | $\bar{x}$ | HG |
| % 8  | 53.510    | B  |
| % 12   | 55.660    | A* |
| LSD $\pm$ 0.7001                               |           |    |
| Varnish type                                   | $\bar{x}$ | HG |
| Alkyd  | 90.210    | A* |
| Two-part polyurethane                          | 36.700    | B  |
| Water-borne                                    | 36.840    | B  |
| LSD $\pm$ 0.8574                               |           |    |
| Thermal processing temperature ( $^{\circ}$ C) | $\bar{x}$ | HG |
| 25   | 55.590    | A* |
| 50   | 54.990    | AB |
| 75   | 54.330    | BC |
| 100  | 53.440    | C  |
| LSD $\pm$ 0.9900                               |           |    |
| Thermal processing time (Days)                 | $\bar{x}$ | HG |
| Control  | 53.060    | D  |
| 25   | 55.870    | A* |
| 50   | 55.390    | AB |
| 75   | 54.240    | C  |
| 100  | 54.370    | BC |
| LSD $\pm$ 0.107                                |           |    |

$\bar{x}$  : Average value HG: The homogeneous group \*: The highest gloss value.

The gloss of the samples with 12% moisture content was determined to be higher than that with 8% moisture content, as shown in Table 9. The gloss was the highest for the alkyd varnish and lower as well as similar for the two-part polyurethane and the water-borne varnishes. The gloss was the highest for the test samples that were treated at 25 °C. The comparison of the thermal processing time indicated that while the gloss value of the control sample was 53.060, the gloss increased on day 25 and 50, whereas the values were slightly lower on day 75 and day 100. The highest gloss was determined on day 25 of thermal ageing.

#### *Eastern beech*

The results of the analysis of variance for the Eastern beech samples are displayed in Table 10.

**Table 10.** Results of Variance Analysis of Eastern Beech Samples

| Source of Variance | Degrees of freedom | Sum of squares | Mean square | F-value     | Prob. $\alpha=0.05$ |
|--------------------|--------------------|----------------|-------------|-------------|---------------------|
| Factor A           | 1                  | 450.081        | 450.081     | 521.8166    | 0.0000              |
| Factor B           | 2                  | 388685.861     | 194342.931  | 225317.8591 | 0.0000              |
| Interaction AB     | 2                  | 112.432        | 56.216      | 65.1760     | 0.0000              |
| Factor C           | 3                  | 8.733          | 2.911       | 3.3749      | 0.0186              |
| Interaction AC     | 3                  | 18.711         | 6.237       | 7.2312      | 0.0001              |
| Interaction BC     | 6                  | 52.101         | 8.683       | 10.0675     | 0.0000              |
| Interaction ABC    | 6                  | 40.175         | 6.696       | 7.7631      | 0.0000              |
| Factor D           | 4                  | 28.084         | 7.021       | 8.1401      | 0.0000              |
| Interaction AD     | 4                  | 6.051          | 1.513       | 1.7539      | 0.1376*             |
| Interaction BD     | 8                  | 184.086        | 23.011      | 26.6783     | 0.0000              |
| Interaction ABD    | 8                  | 21.146         | 2.643       | 3.0645      | 0.0024              |
| Interaction CD     | 12                 | 78.096         | 6.508       | 7.5452      | 0.0000              |
| Interaction ACD    | 12                 | 46.944         | 3.912       | 4.5356      | 0.0000              |
| Interaction BCD    | 24                 | 398.871        | 16.620      | 19.2685     | 0.0000              |
| Interaction ABCD   | 24                 | 102.373        | 4.266       | 4.9454      | 0.0000              |
| Error              | 360                | 310.510        | 0.863       |             |                     |
| Total              | 479                | 390544.257     |             |             |                     |

Factor A: Moisture content, B: Varnish type, C: Thermal processing temperature, D: Thermal processing time \*: Meaningless (according to  $\alpha=0.05$ )

The results of the analysis of variance indicated that all the factors and the factor interactions except for AD were meaningful at a significance level of  $\alpha = 0.05$ . The comparison results of the Duncan test on the factor levels of moisture content, type of varnish, thermal processing temperature, and thermal processing time, which was conducted using the LSD critical value, are displayed in Table 11.

**Table 11.** Comparison Results of Duncan Test of Eastern Beech Samples

| Moisture content                    | $\bar{x}$ | HG |
|-------------------------------------|-----------|----|
| % 8                                 | 52.320    | B  |
| % 12                                | 54.250    | A* |
| LSD $\pm$ 0.1666                    |           |    |
| Varnish type                        | $\bar{x}$ | HG |
| Alkyd                               | 93.480    | A* |
| Two-part polyurethane               | 34.880    | B  |
| Water-borne                         | 31.500    | C  |
| LSD $\pm$ 0.2041                    |           |    |
| Thermal processing temperature (°C) | $\bar{x}$ | HG |
| 25                                  | 53.440    | A* |
| 50                                  | 53.360    | A* |
| 75                                  | 53.260    | AB |
| 100                                 | 53.080    | B  |
| LSD $\pm$ 0.2357                    |           |    |
| Thermal processing time (Days)      | $\bar{x}$ | HG |
| Control                             | 53.550    | A* |
| 25                                  | 53.210    | B  |
| 50                                  | 53.420    | AB |
| 75                                  | 53.390    | AB |
| 100                                 | 52.850    | C  |
| LSD $\pm$ 0.2635                    |           |    |

$\bar{x}$  : Average value HG: The homogeneous group \*: The highest gloss value.

The gloss of the samples with 12% moisture content was determined to be higher, as shown in Table 11. The gloss was the highest for the alkyd varnish and the lowest for the water-borne varnish. The gloss was high for the test samples that were treated at 25 or 50 °C. The comparison of the thermal processing time indicates that while the gloss value of the control sample was 53.550, the gloss slightly decreased in the measurements taken on day 25, whereas the values were slightly higher on day 50 and day 75, decreasing again on day 100.

#### *Sessile oak*

The results of the analysis of variance for the Sessile oak samples are displayed in Table 12. These results indicate that the factors except for factor A and the factor interactions except for AC and ABC were meaningful at  $\alpha = 0.05$ . The comparison results of the Duncan test on the factor levels of moisture content, type of varnish, thermal processing temperature, and thermal processing time, which was conducted using the LSD critical value, are displayed in Table 13.

The gloss was the highest for the alkyd varnish and the lowest for the water-borne varnish. The gloss was high for the test samples that were treated at 25 or 50 °C. The comparison of the thermal processing time indicated that while the gloss value of the control sample was 51.140, the gloss slightly increased until day 50, whereas the values were slightly lower on day 75 and day 100. The highest value for gloss was measured on day 50 of ageing.

**Table 12.** Results of Variance Analysis of Sessile Oak Samples

| Source of Variance | Degrees of freedom | Sum of squares | Mean square | F-value    | Prob. $\alpha=0.05$ |
|--------------------|--------------------|----------------|-------------|------------|---------------------|
| Factor A           | 1                  | 9.213          | 9.213       | 3.6517     | 0.0568*             |
| Factor B           | 2                  | 375371.431     | 187685.716  | 74390.9269 | 0.0000              |
| Interaction AB     | 2                  | 583.685        | 291.843     | 115.6744   | 0.0000              |
| Factor C           | 3                  | 112.504        | 37.501      | 14.8640    | 0.0000              |
| Interaction AC     | 3                  | 8.343          | 2.781       | 1.1023     | 0.3481*             |
| Interaction BC     | 6                  | 129.242        | 21.540      | 8.5377     | 0.0000              |
| Interaction ABC    | 6                  | 25.232         | 4.205       | 1.6668     | 0.1281*             |
| Factor D           | 4                  | 145.575        | 36.394      | 14.4250    | 0.0000              |
| Interaction AD     | 4                  | 31.295         | 7.824       | 3.1010     | 0.0157              |
| Interaction BD     | 8                  | 627.498        | 78.437      | 31.0893    | 0.0000              |
| Interaction ABD    | 8                  | 92.357         | 11.545      | 4.5758     | 0.0000              |
| Interaction CD     | 12                 | 171.646        | 14.304      | 5.6695     | 0.0000              |
| Interaction ACD    | 12                 | 219.584        | 18.299      | 7.2528     | 0.0000              |
| Interaction BCD    | 24                 | 1226.473       | 51.103      | 20.2551    | 0.0000              |
| Interaction ABCD   | 24                 | 273.460        | 11.394      | 4.5162     | 0.0000              |
| Error              | 360                | 908.267        | 2.523       |            |                     |
| Total              | 479                | 379935.806     |             |            |                     |

Factor A: Moisture content, B: Varnish type, C: Thermal processing temperature, D: Thermal processing time \* : Meaningless (according to  $\alpha=0.05$ )

**Table 13.** Comparison Results of Duncan Test of Sessile Oak Samples

|  |           |    |
|--|-----------|----|
| Varnish type                                   | $\bar{x}$ | HG |
| Alkyd  | 91.210    | A* |
| Two-part polyurethane                          | 34.880    | B  |
| Water-borne                                    | 29.300    | C  |
| LSD $\pm$ 0.3489                               |           |    |
| Thermal processing temperature ( $^{\circ}$ C) | $\bar{x}$ | HG |
| 25   | 52.410    | A* |
| 50   | 52.090    | A* |
| 75   | 51.530    | B  |
| 100  | 51.160    | B  |
| LSD $\pm$ 0.4029                               |           |    |
| Thermal processing time (Days)                 | $\bar{x}$ | HG |
| Control  | 51.140    | D  |
| 25   | 51.740    | BC |
| 50   | 52.670    | A* |
| 75   | 52.100    | B  |
| 100  | 51.320    | CD |
| LSD $\pm$ 0.4505                               |           |    |

$\bar{x}$  : Average value HG: The homogeneous group \* : The highest gloss value.

The results of the study indicate that the gloss value increased during the initial days of ageing for the Scots pine and oak wood samples followed by a decrease in gloss in later days of ageing, whereas the opposite situation held true for the eastern beech samples. The highest reduction in gloss was observed in the Scots pine samples. Thermal processes were previously reported to cause changes in the physical and chemical

properties of wood materials and the cause of these changes was shown to be the thermal degradation of hemicellulose. Theoretically speaking, the hydroxyl (OH) groups in hemicellulose are reported to have a profound effect on physical properties of wood. A significant decrease in the amount of hydroxyl groups in the wood material could be observed following thermal treatment (Inoue *et al.* 1993; Boonstra 2008). From this perspective, the reduced gloss in Scots pine samples would have been caused by the thermal degradation of hemicellulose.

Increase in moisture content of the wood material resulted in lowering of the gloss in the conducted study. The gloss of the varnish layers was reported to be dependent mainly on the smoothness of the surface and the ability to reflect light and the existing or acquired water in the wood material would cause swelling of the fibers which in turn would adversely affect the smoothness of the surface reducing gloss (Sönmez *et al.* 2004; Sönmez and Budakçı 2004; Sönmez *et al.* 2011b).

The highest gloss was achieved by using alkyd varnish on the test samples. This situation was thought to be caused by the thermoplastic structure of the oil alkyds used in the manufacture of the alkyd varnishes. The lack of any deformation (cracking, wrinkling, *etc.*) on the flexible alkyd varnish layers following thermal ageing might have resulted in attaining high gloss values.

An increase in the thermal processing temperature and time caused a decrease in the gloss value of the varnish layers. The variations in moisture content and the structural deformations on the varnish molecules during elevated temperatures and prolonged treatment periods were thought to result in this reduction in gloss. The results were in conjunction with the reported literature (Yang *et al.* 2002; Döngel *et al.* 2008).

## CONCLUSIONS

The reduction in gloss and adhesion strength during thermal ageing was determined in the present study and the results regarding the resistance of varnish layers against this effect were discussed. The optimal results were obtained for the Eastern beech test samples with alkyd varnish application.

Generally speaking, the moisture content factor was determined to be insignificant in the evaluation of the adhesion strength of the samples, whereas an increase in moisture content was associated with reduced gloss. The adhesion strength of all thermally-aged samples was lower than that of the control samples, and increases in the thermal processing temperature and time were determined to cause a decrease in gloss values.

In conclusion, application of alkyd varnish on beech material would be the preferred option for furniture and decoration elements that would be exposed to thermal ageing in order to achieve and maintain high surface adhesion and gloss values.

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