

## INFLUENCE OF ACCELERATED AGEING ON MORPHOLOGY AND WETTING OF WOOD SURFACE TREATED WITH A MODIFIED WATER-BASED COATING SYSTEM

Jozef Kúdela – Martina Štrbová – František Jaš

### ABSTRACT

This work evaluates accelerated ageing effects on quality of tree-of-heaven wood surface finished with a water-based coating system applied in several colour hues. This coating system has been adjusted for surface treatment intended for outdoor exposure. There were studied morphological changes in surface of treated wood at accelerated ageing, through its roughness parameters. There was also investigated the resistance of this wood against wetting with liquids and surface free energy with its components.

The results show that the dry accelerated ageing mode did not cause significant changes in roughness and waviness. The wet mode induced moderate increase in roughness, enhancing, in such a way, variability in roughness and waviness. In all cases, the higher roughness and waviness values were recorded perpendicular to the grain. This gives evidence that the surface treatment had not resulted in total smoothing the wood anisotropy.

The experimental results related to wetting with specific liquids also confirmed high water-resistance of the tested coating system. The contact angles occurring during wetting with water exceeded 90°. This ensured effective protection for wood surface against water during ageing, and the overall stability of the system wood solid-coating.

The average surface free energy values of specimens surface-treated with the tested coating system determined based on wood wetting with water and diiodomethane were comparatively low (about 26 mJm<sup>-2</sup>), with dominant apolar component. The dry mode did not induce significant response in surface free energy. The wet (rainfall simulation) mode resulted in a moderate increase in surface free energy (to about 34 mJm<sup>-2</sup>), mostly due to the increase in the polar component.

The colour hue of the coating system had no effects on the investigated characteristics.

**Key words:** surface treatment, wood, coating material, accelerated ageing, colour change, gloss.

### INTRODUCTION

In outdoor conditions, wood surface layers are exposed to radiation, moisture, heat/frost, pollutants and other factors acting in interactions. As such, the surface wood layers are subject to degradation. The first ageing-associated changes are manifested as colour variations induced by degradation of lignin, and to some extent also hemicelluloses. There are species-specific differences in wood chemistry; consequently, there are also differences in the photo-degradation rate among the species (PANDEY and VUORINEN 2008, FAN *et al.* 2010, CHEN *et al.* 2012 and others).

Later, the progressive ageing-related wood surface degradation impairs its morphology. The surface roughness and waviness increase, and the wood surface texture may turn plastic (FEIST 1990, KÚDELA and IHRACKÝ 2014). This is mainly typical for coniferous wood species as the density of their early and late wood differs distinctly. The changes in wood structure are responded by changes in more surface properties (HON 1981, WILLIAMS *et al.* 2001, KISHINO a NAKANO 2004, TOLVAJ *et al.* 2011, HUANG *et al.* 2012, IHRACKÝ 2014, KÚDELA *et al.* 2015).

One of wood surface protection methods against outdoor effects is application of an appropriate coating material. Evidently, the function of wood surface treatment is not only to improve the look but also to protect. In exterior, this protective function should mean mainly inhibiting penetration of UV radiation, rain water and other harmful factors.

In case of surface-treated wood, the early degradation phases cause wood discolouration and gloss reduction (SAHA *et al.* 2013a, OLSSON *et al.* 2014, KÚDELA *et al.* 2016 and others). The discolouration may be due to the degraded coating but also due to the degraded wood surface. Contrarily, the gloss reduction is due to the degraded coating alone (OLLSON *et al.* 2014).

Coatings are also intended to protect wood against water, so the coating resistance against water or also other liquids is a crucial characteristic. The surface wettability with liquids is assessed based on contact angle value – the measure of the tested-material affinity for water. The contact angle values at interface between the surface-treated wood and the standard liquid provide a background for deriving the thermodynamic characteristics of the wetted wood surface – surface free energy with its components and adhesion work (KÚDELA and LIPTÁKOVÁ 2006, PETRIČ a OVENS 2015, HUBBE *et al.* 2015). Different wetting of surface treated wood before and during ageing is close associated with the wood surface degradation (LANDRY and BLANCHETT 2012, SAHA *et al.* 2013a).

The service life of surface treatment depends on the coating performance in reflecting or absorbing UV radiation. Consequently, the surface treatment is improved by adding more pigments, organic absorbers of UV radiation or other specific additives (bark extracts) – SAHA *et al.* (2013a).

The current trends in investigating the ageing of wood surface treated with coating materials aimed to improve its colour stability are several: using nano-particles for coating modification on organic-inorganic base, wood surface pre-treatment with plasma, and similar (LANDRY and BLANCHETT 2012, KOCAEFE and SAHA 2012, SAHA *et al.* 2013a, b, OLSSON *et al.* 2014, WAN *et al.* 2014, GIRARDI *et al.* 2014, REINPRECHT and ŠOMŠÁK 2015).

Our research objective was to study how the accelerated ageing influenced the surface treatment quality. The surface quality changes were assessed through visually observed changes in morphological and physical characteristics of wood surface treated with a water-based coating system. The system was applied in several colour hues, and it was modified for use in outdoor conditions. The work KÚDELA *et al.* (2016) evaluates the accelerated ageing effects on wood decolouration and gloss reduction in wood treated with the coating system. The results show that the system applied was high resistant against photo-degradation, with the colour hue being an important factor.

The aim of this work was to assess how accelerated ageing mimicking outdoor conditions affected the roughness, wetting and surface energy variation in wood surface treated with the relevant coating system.

## MATERIAL AND METHODS

Accelerated ageing was simulated on specimens prepared of 0.5 mm thick veneers of tree of heaven (*Ailanthus altissima*), the specimens size was 80 (L) × 33 (R/T) mm. The

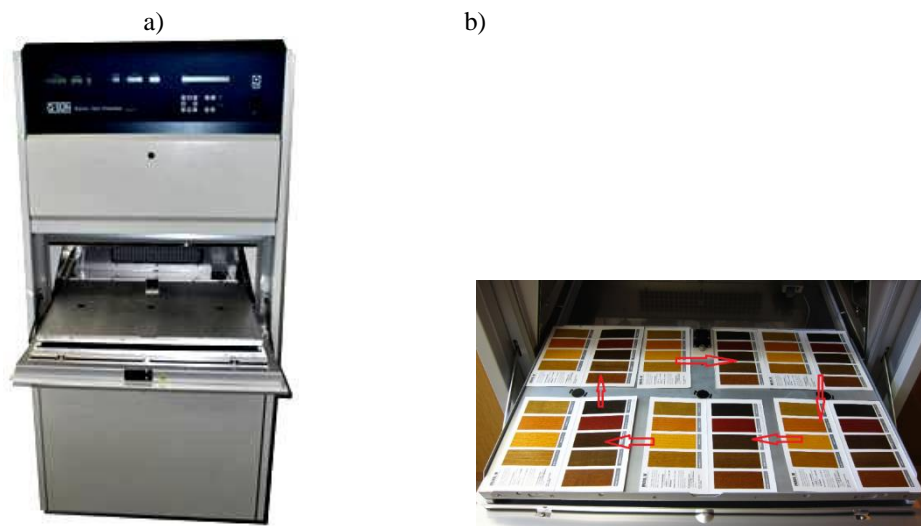
veneers were firstly coated with an impregnation primer varnish Iruxil W-I, adjusted by adding fungicides and insecticides and micronized pigments (iron oxides). The aim was to improve protection against negative UV radiation effects. There were used the following 9 colour hues:

- IRUXIL W-I-500 Natural
- IRUXIL W-I-510 Pine
- IRUXIL W-I-520 Teak
- IRUXIL W-I-530 Oak
- IRUXIL W-I-540 Chestnut
- IRUXIL W-I-550 Walnut
- IRUXIL W-I-560 Dark walnut
- IRUXIL W-I-570 Mahogany
- IRUXIL W-I-580 Ebony

The final coat was a transparent top varnish Iruxil WP-600 Natural intended for outdoor performance. The accelerated wood ageing was simulated in a xenon test chamber Q-SUN Xe-3-HS (Fig. 1a). The average thickness of the primer was 25  $\mu\text{m}$ , the average thickness of the top varnish was 33  $\mu\text{m}$ .

The surface-treated experimental material was arranged equidistantly across the xenon test chamber. To ensure the equal radiation intensity and heat for all the specimens, the specimens were regularly shifted according to a recommended schedule (Fig. 1b).

The ageing conditions in the xenon test chamber followed the standard ASTM G 155. This standard is a fundamental one determining the conditions for accelerated ageing for non-metallic materials with the aid of a xenon discharge tube. Two modes for outdoor conditions were chosen: „dry“ (without water) mode and „wet“ (rainfall simulation). The first mode simulates outdoor conditions in case when wood is exposed to UV radiation but protected from rain water, the second simulates conditions when wood is exposed to both factors, UV and rain. The test parameters are in Tables 1 and 2.



**Fig. 1 Xenon test chamber Q-SUN Xe-3-HS and specimens rotation layout during accelerated ageing.**

The radiation intensity was  $0.35 \text{ W} \cdot \text{m}^{-2}$  with a radiation wave length of 340 nm, following the Standard. This value corresponds to the mean annual value for the temperate zone. The temperature, controlled on a black panel, corresponds to the maximum temperature on the panel surface. In both modes, one accelerated ageing cycle consisted of two steps, covering altogether 120 min (102 and 18). The ageing process represented 250 cycles, 500 hours in total (Tables 1 and 2).

**Tab. 1 The ageing parameters set according to the Standard ASTM G 155 “water-free mode”.**

| Step | Mode           | Radiation intensity (W/m <sup>2</sup> ) | Black panel temperature (°C) | Air temperature (°C) | Relative air humidity (%) | Time (min.) |
|------|----------------|---|------------------------------|----------------------|---------------------------|-------------|
| 1    | Radiation      | 0.35                                    | 63                           | 48                   | 30                        | 102         |
| 2    | Radiation-free | -                                       | -                            | 38                   | –                         | 18          |

**Tab. 2 The ageing parameters set according to the Standard ASTM G 155 “wet mode”.**

| Step | Mode                       | Radiation intensity (W/m <sup>2</sup> ) | Black panel temperature (°C) | Air temperature (°C) | Relative air humidity (%) | Time (min.) |
|------|----------------------------|---|------------------------------|----------------------|---------------------------|-------------|
| 1    | Radiation                  | 0.35                                    | 63                           | 48                   | 30                        | 102         |
| 2    | Radiation + water spraying | 0.35                                    | 63                           | 48                   | 90                        | 18          |

### Roughness and waviness measurements

The roughness and waviness profiles of wood surface finished with the discussed coating system were scanned with a Surfcom 130 A (Fig. 2). The roughness was measured in each specimen, parallel to and perpendicular to the grain, at two measuring spots in the two anatomical directions. The sampling length was 2.5 mm; the evaluation length was 25 mm.



**Fig. 2 Surfcom 130 A.**

There were investigated two basic roughness parameters – arithmetic mean deviation of the roughness profile ( $R_a$ ) and the maximum height of the assessed profile ( $R_z$ ). The mean arithmetic deviation of the roughness profile ( $R_a$ ) represents the mean arithmetic values of absolute profile deviations  $Z(x)$  over the range of sampling length, i.e.

$$R_a = \frac{1}{l} \int_0^l |Z(x)| dx \quad (1)$$

where  $l$  is the sampling length and  $Z$  is the distance of the scanned spot at the distance  $x_i$  from the centre profile line, within the evaluation length.

The maximum height of roughness profile ( $R_z$ ) was determined as the sum of the highest profile peaks  $Z_p$  and the deepest profile valleys  $Z_v$  within the sampling length

$$R_z = \max Z_{pi} + \max Z_{vi}. \quad (2)$$

The waviness profile was assessed based on the parameter  $Wa$ . The roughness and waviness were measured prior to the ageing and after 500h ageing, in the two ageing modes.

### Contact angle measurements

The surface treated specimens were wetted with two liquids – diiodomethane (apolar liquid) and redistilled water (polar-apolar liquid). The liquids were chosen as suggested in KÚDELA (2014). The surface free energy, and its disperse and polar component values for the two tested liquids are in Table 3.

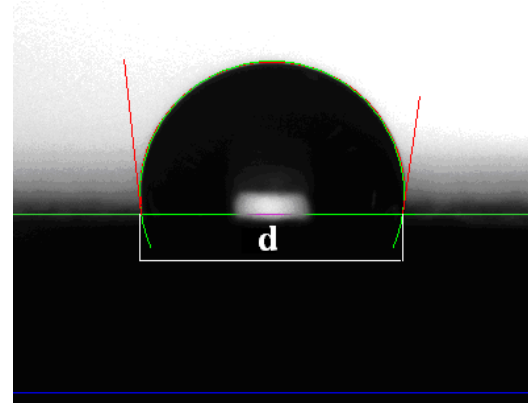
**Tab. 3 Surface free energy of the used liquids  $\gamma_L$ , disperse and polar components  $\gamma_L^d$  and  $\gamma_L^p$ .**

| Testing liquid | $\gamma_L$ [ $\text{mJ}\cdot\text{m}^{-2}$ ] | $\gamma_L^d$ [ $\text{mJ}\cdot\text{m}^{-2}$ ] | $\gamma_L^p$ [ $\text{mJ}\cdot\text{m}^{-2}$ ] |
|----------------|--|--|--|
| Water          | 72.80  | 21.80  | 51.00  |
| Diiodomethane  | 50.80  | 50.80  | 0.00   |

As in the former case, the surface wetting was investigated prior starting and after finishing the ageing process. We used a goniometer *Krüß DSA30 Standard* (Fig. 3) with the accessory software *DSA3* for drop shape analysis.



**Fig. 3 Goniometer Krüss DSA30 Standard.**



**Fig. 4 Drop contact angle determined by circle method.**

The drop was applied in a volume of 0.0018 ml. Then, its shape was scanned parallel to the grain, for 60 seconds. The contact angles were determined by the Circle method, and, at the same time, the drop diameter  $d$  was measured (Fig. 4).

### Determining surface free energy

The surface free energy of surface treated wood  $\gamma_S$  was calculated using the adjusted equation by Neumann *et al.* (1974)

$$\cos \theta = \frac{(0,013\gamma_S - 2,00)\sqrt{\gamma_S\gamma_L} + \gamma_L}{\gamma_L(0,013\sqrt{\gamma_S\gamma_L} - 1)} \quad (3)$$

The surface free energy of surface treated wood was determined separately for wetting with water and for wetting with diiodomethane. In this case, the equilibrium state could not be determined according to LIPTÁKOVÁ and KÚDELA (1994), so the surface free energy values

were calculated based on contact angle values  $\theta_0$  measured immediately after the drop application.

The disperse and polar components of the surface free energy  $\gamma_s^d$  and  $\gamma_s^p$  were calculated according to KLOUBEK (1974), based on contact angle values and based on the acknowledged values of disperse and polar component of surface free energy of the test liquids  $\gamma_L^d$  and  $\gamma_L^p$ :

$$\sqrt{\gamma_s^d} = \sqrt{\gamma_L^d} \frac{1 + \cos \theta}{2} \pm \sqrt{\gamma_L^p} \sqrt{\frac{\gamma_s}{\gamma_L} - \left(\frac{1 + \cos \theta}{2}\right)^2} \quad (4)$$

$$\sqrt{\gamma_s^p} = \sqrt{\gamma_L^p} \frac{1 + \cos \theta}{2} \mp \sqrt{\gamma_L^d} \sqrt{\frac{\gamma_s}{\gamma_L} - \left(\frac{1 + \cos \theta}{2}\right)^2} \quad (5)$$

The results of surface free energy of surface treated wood were compared with the results obtained by methods described in FOWKES (1967) and OWENS and WENDT (1969).

## RESULTS AND DISCUSSION

### Roughness and waviness

The assessment results for morphology of wood surface finished with the studied coating system are summarised in Fig. 5. The assessment was made through roughness parameters  $Ra$ ,  $Rz$  and waviness parameter  $Wa$  by comparing their values before and after the accelerated ageing process, between water-free and dry mode and between the parallel to grain and perpendicular to grain anatomical direction. The results of a two-way ANOVA did not confirm significant influence of 500h ageing on the waviness or the roughness parameters. On the other hand, after finishing the ageing process, there was observed an increased variability in the parameter  $Rz$  perpendicular to grain. There was also identified significant influence of anatomical direction. Significantly higher roughness parameters were measured perpendicular to grain (Fig. 5). This means that the surface treatment had not suppressed wood anisotropy completely. The surface of the coating system mimicked to some extent the original structure of the tree of heaven wood.

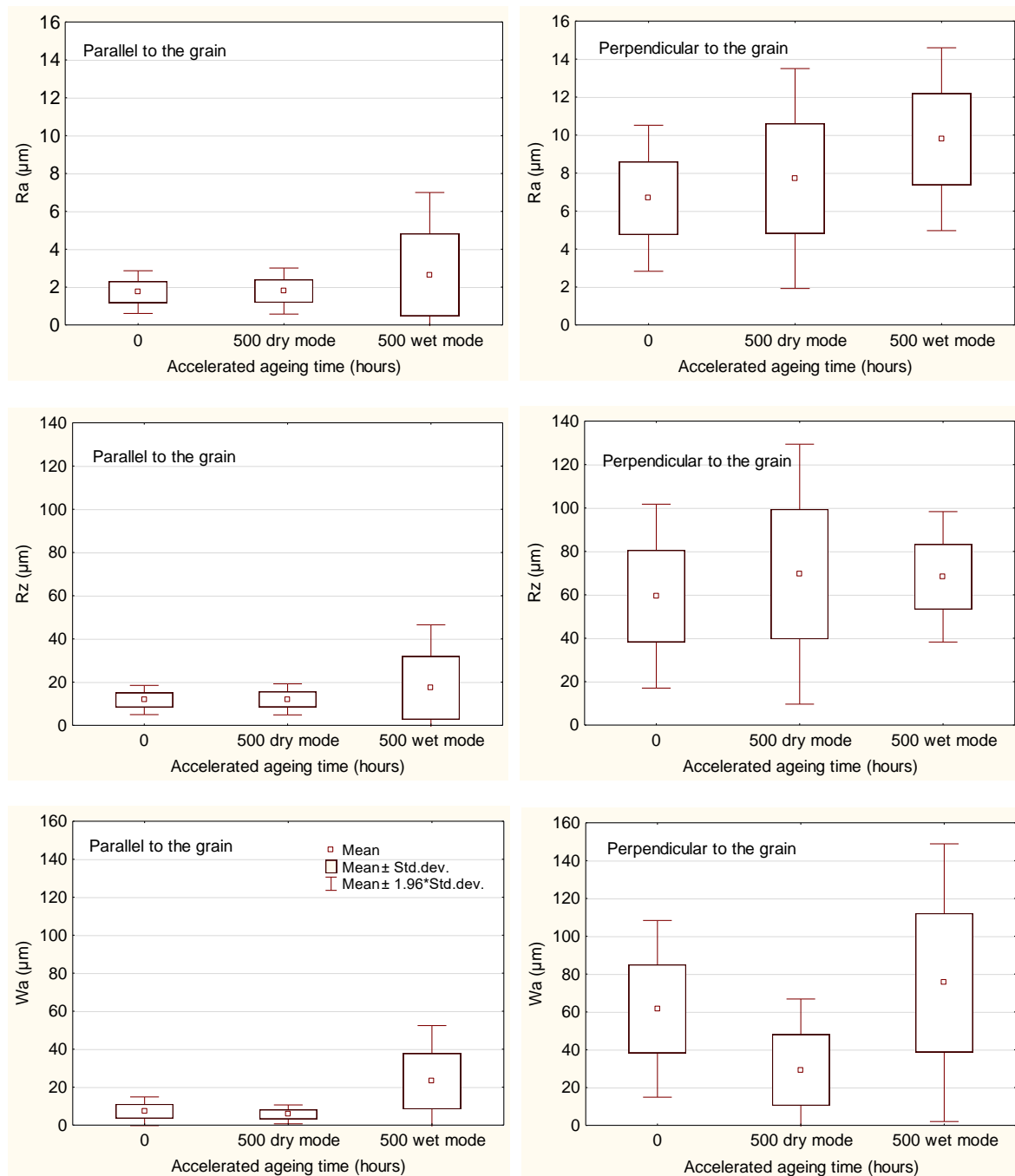
After 500h ageing in the wet mode, there was observed an increasing trend in roughness. The increase was most conspicuous in case of parameter  $Ra$  perpendicular to the grain. At the same time, there increased variability of roughness parameters values parallel to the grain (Fig. 5).

KÚDELA and IHRACKÝ (2012) show that under the same ageing conditions, wood roughness in untreated wood significantly increases. This means that the relevant surface treatments was high resistant against degradation effects induced by UV radiation and water in mutual interaction. Simultaneously, the surface treatment provided protection of wood surface against these degradation effects. In our case, the roughness variability was not as obvious as reported by Van den BLUCKE *et al.* (2007) who investigated roughness parameters variability in five surface treatment types subject to 200 ageing cycles.

The values of waviness parameter  $Wa$  were significantly lower in the direction parallel to the grain than perpendicular to the grain. In the case of the dry mode, the waviness after the ageing was somewhat lower than before the ageing, in both anatomic directions. In the case of the wet regimen, the waviness increased in both directions, with the  $Wa$  values displaying more variability. The variability was apparent mainly perpendicular to the grain (Fig. 5).

During accelerated ageing in the wet mode, the moisture content increased due to transverse buckling of specimens. This buckling was caused by varying moisture migration

through untreated surfaces during individual ageing cycles. The transverse buckling also initiated minute fissures progressing later into the coating, which resulted in variability increase of the roughness and waviness parameters.

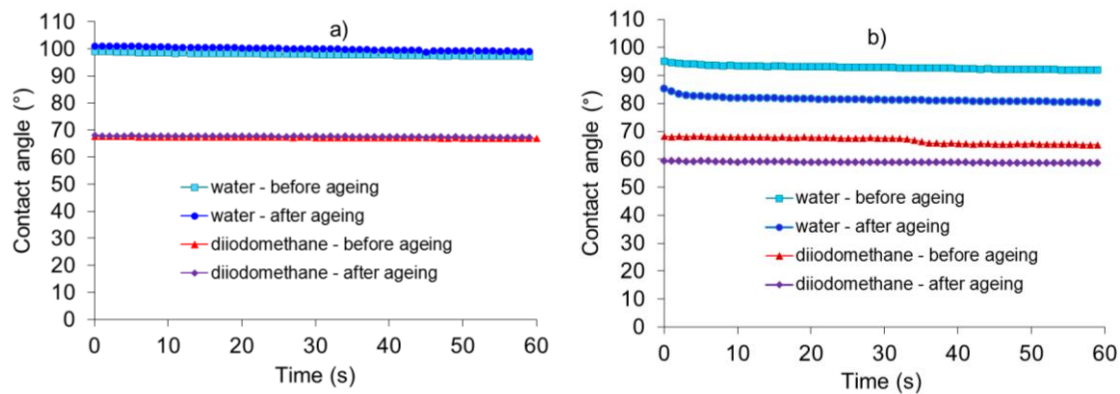


**Fig. 5 Accelerated ageing effects on roughness and waviness parameters.**

### Wood surface wetting

The wetting power of the test liquids on the specimens' surface covered with the investigated coating system was assessed based on the contact angle values measured before the accelerated ageing and after the 500h ageing process. The typical variation in the contact angles measured during one minute from the first test liquid contact with the treated surface is illustrated in Fig. 6. The mean contact angle values  $\theta_0$  and  $\theta_{60}$  (at the moment of the first contact and after 60s wetting) together with other statistical variables are presented in Table 4.

The results show that during wetting with water, the contact angle values were bigger than 90° over all the wetting process. This ascertains the high resistance of the surface treatment against water. Such surfaces may be declared as imperfect water-repellent. The contact angle values did not display noticeable changes even after 500h treatment under the water-free regimen. This means that the surface treatment maintained fairly water-resistant during all the ageing process.



**Fig. 6** Contact angles varying during the wetting process of surface treated specimens before and after 500h accelerated ageing; a) water-free regimen, b) wet regimen.

**Tab. 4** Basic statistical characteristics of the contact angle values at the moment of application –  $\theta$  and after 60s water-wetting process –  $\theta_{60}$  in surface treated wood before and after accelerated ageing.

| Basic statistical characteristics | Contact angle $\theta$             |           | Contact angle $\theta_{60}$ |           | Contact angle $\theta$             |           | Contact angle $\theta_{60}$ |           |
|-----------------------------------|------------------------------------|-----------|-----------------------------|-----------|------------------------------------|-----------|-----------------------------|-----------|
|                                   | Accelerated ageing time – dry mode |           |                             |           | Accelerated ageing time – wet mode |           |                             |           |
|                                   | 0 hours                            | 500 hours | 0 hours                     | 500 hours | 0 hours                            | 500 hours | 0 hours                     | 500 hours |
|                                   | Water                              |           |                             |           |                                    |           |                             |           |
| <b>x</b> (°)                      | 99.2                               | 101.2     | 97.2                        | 99.0      | 93.9                               | 84.8      | 91.6                        | 80.9      |
| <b>s</b> (°)                      | 1.2                                | 1.0       | 1.4                         | 1.2       | 1.8                                | 4.8       | 1.8                         | 5.2       |
| <b>v</b> (%)                      | 1.3                                | 1.0       | 1.4                         | 1.2       | 1.9                                | 5.6       | 1.9                         | 6.5       |
| <b>n</b>                          | 36                                 | 36        | 36                          | 36        | 36                                 | 36        | 36                          | 36        |
|                                   | Diiodomethane                      |           |                             |           |                                    |           |                             |           |
| <b>x</b> (°)                      | 67.7                               | 68.1      | 67.9                        | 68.0      | 68.2                               | 59.4      | 63.6                        | 58.7      |
| <b>s</b> (°)                      | 4.4                                | 4.4       | 3.5                         | 4.1       | 3.0                                | 3.0       | 2.9                         | 3.0       |
| <b>v</b> (%)                      | 6.6                                | 6.4       | 5.1                         | 6.0       | 4.4                                | 5.0       | 4.5                         | 5.1       |
| <b>n</b>                          | 36                                 | 36        | 36                          | 36        | 36                                 | 36        | 36                          | 36        |

In case of the wet (rainfall simulation) accelerated ageing mode, the contact angle values ranged from 80°–85°. The more extensive wetting may be due to micro-fissures progressing from the substrate to the coating as the result of the transverse veneer buckling. The coating by itself was water-resistant even after the wet ageing process.

Wood wetting with the test apolar liquid (diiodomethane) was more extensive than with water, compelled by interactions among unsaturated apolar forces occurring in the initial phase of the wetting process, mostly immediately after the first contact between diiodomethane and substrate (KÚDELA 2014). The average contact angle values ranged from 63° to 68°. After 500h ageing (dry regimen), there were no obvious changes in wood wetted with diiodomethane. In the case of wet accelerated ageing, the diiodomethane contact angle values showed decrease analogically to the water contact angle values (Table 4).



Qualitatively similar values were obtained by LANDRY and BLANCHETT (2012). These authors investigated the accelerated ageing effects on water-wetting of pine wood surface treated with two types of acrylate coats. Their wetting liquid was water, nevertheless, their results were quantitatively similar to the results we acquired with diiodomethane.

SAHA *et al.* (2013a) investigated pine thermo-wood coated with polyurethane-acrylate coat containing CeO<sub>2</sub> nanoparticles. The contact angle values obtained for water after artificial ageing were higher than the original ones, however, in all cases significantly lower than 90°.

As the wetting of surface-treated wood is modified due to wood surface degradation caused by ageing (LANDRY and BLANCHETT 2012, SAHA *et al.* 2013a), in our case we may declare that the water-free ageing mode did not initiate surface degradation, and the surface maintained an effective barrier against water penetration into the internal wood structure. In the case of the wet mode, the contact angle changes were small, which provide evidence for minimum degradation of the coating also in this case.

### Surface free energy

The values of surface free energy with its disperse and polar components were calculated from the Equations (3), (4), (5), separately for water and diiodomethane. These values are presented in Tables 5 and 6, together with the surface free energy values obtained according to KÚDELA (2014) and Fowkes (FOWKES 1967, OWENS and WENDT 1969). In all cases, the surface free energy was calculated based on the contact angle values  $\theta_0$  measured immediately after the liquid application on the surface. Unlike in the native wood surface, the drop profile diameter  $d$  did not vary; consequently, the equilibrium state was not possible to determine by the methods designed by LIPTÁKOVÁ and KÚDELA (1994). Our decision for  $\theta_0$  was also supported by the fact that the contact angle values did not vary significantly over the time related.

The average surface free energy values for specimen surface treated with the tested coating system ranged, in all calculation modes from 20 to 27 mJm<sup>-2</sup>. In all cases, the apolar component was dominant. The results show (Table 5) that different liquid standards used for determining thermodynamic characteristics at the interface between wood and coating material behaved differently. This was then reflected in different values of surface free energy and its components.

In the case of the coated wood, the surface free energy values were considerably lower than the surface free energy values of various wood species without surface treatment reported by several authors using several methods and summarised by GINDL (2002).

Values were also lower than the values of solid coating films formed from several lacquer types reported by KÚDELA and LIPTÁKOVÁ (2006). These authors declare an increase in the surface free energy of coating films after their hardening (drying). It follows that the surface free energy of the original liquid coating system needed to be lower, which facilitated the coat spreading over the wood surface with good adhesion properties. In our opinion, this is the cause underlying the high stability of the tested coating system during the ageing process.

After applying the dry mode, the surface free energy did not display significant variation. In the case of wet mode, the surface free energy values increased, mostly due to the polar component increase.

The final surface free energy values were obtained by adding the disperse component values calculated according to the Equation (4) with using diiodomethane to the polar component values calculated according to the Equation (5) using water. The free surface energy values obtained in this way were practically the same as the values stated according to Fowkes. The differences did not reach beyond the variability within these characteristics.

**Tab. 5 Surface free energy and its components values for surface-treated specimens before and after ageing process, dry mode, several different methods.**

| Basic statistical characteristics  | From Equations (3), (4), (5)       |           |               |           | KÚDELA 2014 |           | FOWKES (1967)<br>OWENS, WENDT (1969) |           |
|------------------------------------|------------------------------------|-----------|---------------|-----------|-------------|-----------|--------------------------------------|-----------|
|                                    | Water                              |           | Diiodomethane |           |             |           |                                      |           |
|                                    | Accelerated ageing time – dry mode |           |               |           |             |           |                                      |           |
|                                    | 0 hours                            | 500 hours | 0 hours       | 500 hours | 0 hours     | 500 hours | 0 hours                              | 500 hours |
| $\gamma_s$ (mJ.m <sup>-2</sup> )   | 21.48                              | 20.20     | 26.93         | 26.71     | 26.14       | 25.63     | 25.3                                 | 24.7      |
| $s$ (mJ.m <sup>-2</sup> )          | 0.81                               | 0.66      | 2.25          | 2.22      | –           | –         | –                                    | –         |
| $v$ (%)                            | 3.76                               | 3.25      | 8.37          | 8.32      | –           | –         | –                                    | –         |
| $n$                                | 36                                 | 36        | 36            | 36        | –           | –         | –                                    | –         |
| $\gamma_s^d$ (mJ.m <sup>-2</sup> ) | 19.54                              | 18.53     | 24.21         | 23.96     | 24.21       | 23.96     | 24.2                                 | 23.9      |
| $s$ (mJ.m <sup>-2</sup> )          | 0.64                               | 0.53      | 2.51          | 2.47      | –           | –         | –                                    | –         |
| $v$ (%)                            | 3.26                               | 2.85      | 10.38         | 10.29     | –           | –         | –                                    | –         |
| $n$                                | 36                                 | 36        | 36            | 36        | –           | –         | –                                    | –         |
| $\gamma_s^p$ (mJ.m <sup>-2</sup> ) | 1.93                               | 1.67      | 2.72          | 2.74      | 1.93        | 1.67      | 1.1                                  | 0.8       |
| $s$ (mJ.m <sup>-2</sup> )          | 0.17                               | 0.13      | 0.26          | 0.25      | –           | –         | –                                    | –         |
| $v$ (%)                            | 8.79                               | 7.61      | 9.57          | 9.00      | –           | –         | –                                    | –         |
| $n$                                | 36                                 | 36        | 36            | 36        | –           | –         | –                                    | –         |

**Tab. 6 Surface free energy and its components values for surface-treated specimens before and after ageing process, wet mode, several different methods.**

| Basic statistical characteristics  | From Equations (3), (4), (5)       |           |               |           | KÚDELA (2014) |           | FOWKES (1967)<br>OWENS, WENDT (1969) |           |
|------------------------------------|------------------------------------|-----------|---------------|-----------|---------------|-----------|--------------------------------------|-----------|
|                                    | Water                              |           | Diiodomethane |           |               |           |                                      |           |
|                                    | Accelerated ageing time – wet mode |           |               |           |               |           |                                      |           |
|                                    | 0 hours                            | 500 hours | 0 hours       | 500 hours | 0 hours       | 500 hours | 0 hours                              | 500 hours |
| $\gamma_s$ (mJ.m <sup>-2</sup> )   | 25,07                              | 31.47     | 26.6          | 31.15     | 26.7          | 33.82     | 26.3                                 | 34.4      |
| $s$ (mJ.m <sup>-2</sup> )          | 1.22                               | 3.42      | 1.53          | 1.49      | –             | –         | –                                    | –         |
| $v$ (%)                            | 4.86                               | 10.88     | 5.73          | 4.80      | –             | –         | –                                    | –         |
| $n$                                | 36                                 | 36        | 36            | 36        | –             | –         | –                                    | –         |
| $\gamma_s^d$ (mJ.m <sup>-2</sup> ) | 22.28                              | 26.59     | 23.91         | 28.95     | 23.91         | 28.95     | 23.9                                 | 28.9      |
| $s$ (mJ.m <sup>-2</sup> )          | 0.89                               | 2.17      | 1.69          | 1.70      | –             | –         | –                                    | –         |
| $v$ (%)                            | 4.01                               | 8.16      | 7.07          | 5.86      | –             | –         | –                                    | –         |
| $n$                                | 36                                 | 36        | 36            | 36        | –             | –         | –                                    | –         |
| $\gamma_s^p$ (mJ.m <sup>-2</sup> ) | 2.79                               | 4.87      | 2.76          | 2.20      | 2.79          | 4.87      | 2.4                                  | 5.5       |
| $s$ (mJ.m <sup>-2</sup> )          | 0.33                               | 1.26      | 0.16          | 0.20      | –             | –         | –                                    | –         |
| $v$ (%)                            | 11.70                              | 25.82     | 5.85          | 9.28      | –             | –         | –                                    | –         |
| $n$                                | 36                                 | 36        | 36            | 36        | –             | –         | –                                    | –         |

The results have confirmed that the interactions among surface forces during wetting a surface-treated wood with an apolar liquid (diiodomethane) occur at the beginning of the wetting process, mostly immediately after the first contact between the liquid and the substrate. In addition to dispersion forces, polar forces act over the interface between wood and polar-apolar liquid (water). Also in this case, the apolar forces interact at the beginning of the wetting process, the polar forces, on the other hand, enter in action gradually (KÚDELA 2014).

The colour hue of the coating system did not affect significantly roughness, wetting and surface free energy associated to ageing. This parameter only affected the colour stability (KÚDELA *et al.* 2016).

## CONCLUSION

The study objective was testing the efficacy of the relevant coating system for resistance of tree-of-heaven veneers subject to accelerated ageing simulating outdoor conditions. There were evaluated surface roughness, wetting performance and changes in surface free energy. The obtained results allow us to derive the following conclusions:

The dry accelerated ageing mode did not cause significant changes in roughness and waviness. The wet mode induced moderate increase in roughness, enhancing, in such a way, variability in roughness and waviness. In all cases, the higher roughness and waviness values were recorded perpendicular to the grain. This gives evidence that the surface treatment had not resulted in total smoothing the wood anisotropy.

The water resistance of the tested coating system has been confirmed by experimental results obtained with wetting specimens surface-treated with specific liquids. The contact angles occurring during wetting with water exceeded 90°. This ensured effective protection for wood surface against water during ageing, and the overall stability of the system wood solid-coating.

The average surface free energy values of specimens surface-treated with the tested coating system determined based on wood wetting with water and diiodomethane were comparatively low (about 26 mJm<sup>-2</sup>), with dominant apolar component. The dry mode did not induce significant response in surface free energy. The wet (rainfall simulation) mode resulted in a moderate increase in surface free energy (to about 34 mJm<sup>-2</sup>), mostly due to the increase in the polar component.

The colour variability of the coating system had no effects on roughness, wetting performance and surface free energy values.

## LITERATURE

- VAN den BLUCKE, J., VAN ACKER, J., SAVEYN, H., STEVENS, M. 2007. Modelling film formation and degradation of semi-transparent exterior wood coatings. *Prog. Org. Coat.*, 58: 1–12.
- FAN, Y., GAO, J., CHEN, Y. 2010: Colour responses of black locust (*Robinia pseudoacacia* L.) to solvent extraction and heat treatment. *Wood Sci. Technol.*, 44: 667–678.
- FEIST, W. C. 1990. Outdoor wood weathering and protection. In Rowell, R.M. and Barbour, J.R (Eds.), *Archaeological Wood Properties, Chemistry, and Preservation*. Washington DC: *Advances in Chemistry Series 225*. Proceedings of 196th meeting, American Chemical Society,
- FOWKES, F. M. 1967. Molecular forces and interfaces. *Surfaces and coatings related to paper and wood*, (Eds. Marchessault, R.H. a Skaar, Ch.) Syracuse University Press, Syracuse, New York, pp. 99–125.
- GINDL, M. 2002. Effects free surface energy on the coating properties of wood (Doctoral Thesis). Vienna: Universitet für Bodenkultur Wien, 68 p.
- GIRARDI, F., CAPPELLETTOA, E., SANDAK, J. *et al.* 2014. Hybrid organic–inorganic materials as coatings for protecting wood. *Progress Org. Coat.*, 77(2): 449–457.
- HON, D. N. 1981. Photochemical degradation of lignocellulosic materials. In Grassie, N (Ed.), *Developments in Polymer Degradation–3*. Essex: Applied Science Ltd. Chapter 8, p. 229–281.

- HUANG, X., KOCAEFE, D., KOCAEFE, Y., BOLUK, Y., PICHETTE, A. 2012. A spectrophotometric and chemical study on color modification of heat-treated wood during artificial weathering. *Applied Surf. Sci.*, 258(14): 5360–5369.
- HUBBE, M. A., GARDNER, D. J., SHEN, W. 2015. Contact Angles and Wettability of Cellulosic Surfaces: A Review of Proposed Mechanisms and Test Strategies. *BioResources*, 10(4): 1–93.
- CHEN, Y., GAO, J., FAN, Y., TSCHABALALA, M. A., STARK, N.M. 2012. Heat-induced chemical and color changes of extractive-free black locust (*Robinia pseudoacacia*) wood. *BioResources*, 7(2): 2236–2248
- KISHINO, M., NAKANO, T. 2004. Artificial weathering of tropical woods. Part 1: Changes in wettability. *Holzforschung*, 58(5): 552–557.
- KOCAEFE, D., SAHA, S. 2012. Comparison of the protection effectiveness of acrylic polyurethane coatings containing bark extracts on three heat-treated North American wood species: Surface degradation. *Appl. Surf. Sci.*, 258(13): 5283–5290.
- KLOUBEK, J. 1974. Calculation of Surface Free Energy Components of ice according to its wettability by water, chlorobenzene and carbon disulfide. *J. Colloid Interface Sci.*, 46: 185–190.
- KÚDELA, J. 2014: Wetting of wood surface by liquids of a different polarity. *Wood Research*, 59(1): 11–24.
- KÚDELA, J., IHRACKÝ, P. 2014: Influence of diverse conditions during accelerated ageing of beech wood on its surface roughness. *Acta Facultatis Xylogiae*, 56(2): 37–46.
- KÚDELA, J., LIPTÁKOVÁ, E. 2006: Adhesion of coating materials to wood. *J. Adhesion Sci. Technol.*, 20(8): 875–895.
- KÚDELA, J., ŠMÍRA, P., MRENICA, L., NASSWETTROVÁ, A., IHRACKÝ, P. 2015. Surface treatment of wood structural elements with dry ice and its influence on wood surface properties. *J. Civil Eng. Architect. Res.*, 2(10): 1002–1010.
- KÚDELA, J., ŠTRBOVÁ, M., JAŠ, F. 2016. Influence of accelerated ageing on colour and gloss changes in tree of heaven surface treated with an iruxil coating system. *Acta Facultatis Xylogiae*, 58(1): 25–34.
- LANDRY, V., BLANCHETT, P. 2012. Weathering resistance of opaque PVDF-acrylic coatings applied on wood substrates. *Progress Org. Coat.* 75(4): 494–501.
- LIPTÁKOVÁ, E., KÚDELA, J. 1994. Analysis of wood-wetting process. *Holzforschung*, 48(2): 139–144.
- NEUMANN, A. W., GOOD, R. J., HOPPE, C. J., SEJPAL, M. 1974. An equation of state approach to determine surface tensions of low-energy solids from contact angles. *J. Colloid Interface Sci.*, 49(2): 291–303.
- OLSSON, S. K., JOHANSSON, M., WESTIN M. *et al.* 2014. Reactive UV-absorber and epoxy functionalized soybean oil for enhanced UV-protection of clear coated wood. *Polym. Degrad. Stab.*, 110: 405–414. doi:10.1016/j.polymdegradstab.2014.09.017.
- OWENS, D. K., WENDT R. C. 1969. Estimation of the surface free energy of polymers. *Appl. Polym. Sci.*, no. 13:1741–1747.
- PANDEY, K. K., VUORINEN, T. 2008. Comparative study of photodegradation of wood by a UV laser and a xenon light source. *Polym. Degrad. Stab.* 93: 2138–2146.
- PETRIČ, M., OVEN, P. 2015: Determination of Wettability of Wood and Its Significance in Wood Science and Technology: A Critical Review. *Reviews of Adhesion and Adhesives*, 2: 121–187.
- REINPRECHT, L., ŠOMŠÁK, M. 2015. Effect of plasma and UV-additives in transparent coatings on the colour stability of spruce (*Picea abies*) wood at its weathering in xenotest. *Acta Facultatis Xylogiae Zvolen.* 57(2): 49–59.
- SAHA, S., KOCAEFE, D., BOLUK, Y., PICHETTE, A. 2013a. Surface degradation of CeO<sub>2</sub> stabilized acrylic polyurethane coated thermally treated jack pine during accelerated weathering. *Applied Surf. Sci.* 276: 86–94.
- SAHA, S., KOCAEFE, D., KRAUSE, C. *et al.* 2013b. Enhancing exterior durability of heat-treated jack pine by photo-stabilization by acrylic polyurethane coating using bark extract. Part 2: Wetting characteristics and fluorescence microscopy analysis. *Progress Org. Coat.* 76: 504–512.
- TOLVAJ, L., FAIX, O. 1996. Modification of colour by steaming. In: *Proceedings of the 2nd international conference on the development of wood science/technology and forestry*. Sopron: University of Sopron, p. 1–10.

TOLVAJ, L., PERSZE, L., ALBERT, L. 2011. Thermal degradation of wood during photodegradation. *J. Photoch. Photobio. B* 105(1): 90–93.

WILLIAMS, R.S., KNAEBE, M. T., EVANS, J., FEIST, W. C. 2001. Erosion rates of wood during natural weathering: Part III. Effect of exposure angle on erosion rate. *Wood Fiber Sci.*, 33(1): 50–57.

WAN, C., LU, Y., SUN, Q., LI, J. 2014. Hydrothermal synthesis of zirconium dioxide coating on the surface of wood with improved UV resistance. *Applied Surf. Sci.*, 321: 38–42.

## **ACKNOWLEDGEMENT**

We highly acknowledge the support from the Scientific Grant Agency of the Ministry of Education SR and the Slovak Academy of Sciences (Grant No. 1/0822/17 „Surface modification of wood and coating materials in order to improve stability of the wood – coating material system“). The authors also express their thanks to Ing. Anton Briš for his assistance at the experimental work.

## **ADDRESSES OF AUTHORS**

Prof. Ing. Jozef Kúdela, CSc.  
Ing. Martina Štrbová, PhD.  
Technical University in Zvolen  
Faculty of Wood Sciences and Technology  
Department of Wood Science  
T. G. Masaryka 24  
960 53 Zvolen  
Slovakia  
kudela@tuzvo.sk  
strbovam@gmail.com

Ing. František Jaš, CSc.  
RENOJAVA, s.r.o.  
Bulharská 26  
080 01 Prešov  
Slovakia  
jas@renojava.sk

