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ACCELERATED-AGEING-INDUCED PHOTO-DEGRADATION OF BEECH WOOD SURFACE TREATED WITH SELECTED COATING MATERIALS

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ABSTRACT

The aim of this work was to assess the colour response of beech wood surface coated with commercially manufactured transparent coating materials, during accelerated ageing process in indoor conditions. There was also tested the impact of beech wood surface pre-treatment with a colorant-based mordant.

The measured and calculated values revealed that the major colour changes occurred during the first 100 hours of the accelerated ageing process. The lacquer types used varied according to their success to protect wood surface against UV radiation effects. The lacquers without protective agents against UV radiation could not inhibit beech wood photo-degradation when applied on this wood. Oppositely, the colour changes were even more pronounced than in case of the native wood. This was due to the photo-degradation of the coating material and of the wood surface.

Protective agents against UV radiation added into coating materials had significant retarding effects on photo-degradation of the surface-treated wood. Positive impact on colour stability of wood surface treated with the tested lacquers was also found for the pre-treatment with a mordent manufactured based on special light-resistant colorants.

Key words: beech wood, accelerated ageing, lacquers, surface treatment, colour, photo-degradation.

INTRODUCTION

Wood is an organic material and as such, in outdoor conditions, it is exposed to degradation process due to synergic effects of various radiation types, moisture, temperature and emitted materials. Important agent in this process is UV radiation.The first alterations associated with wood ageing process are colour changes due to photo-degradation of lignin and to some extent also hemicelluloses (PANDEY a VUORINEN 2008, FAN *et al.* 2010, CHEN *et al.* 2012, KUBOVSKÝ and KAČÍK 2013, 2014). Other important agents are UV sensitive extractive substances (CHANG *et al.* 2010, PERSZE and TOLVAJ 2012). These substances can react with hydrocarbons or with the products of lignin hydrolysis and form lignin-similar compounds (TOLVAJ and FAIX 1996).

If ageing conditions rule for long, the colour changes are followed by additional wood surface degradation affecting negatively wood morphology and other surface properties (HON 1981, WILIAMS *et al.* 2001, KISHINO a NAKANO 2004, TOLVAJ *et al.* 2011, HUANG *et al.* 2012, IHRACKÝ 2014, KÚDELA *et al.* 2015).

The most common wood surface protection is treatment with coating materials promising powerful protection against adverse effects of external factors. Expected is also protection of wood colour stability, and its resistance to light-induced changes. This is ensured by inhibition of UV penetration to lignin and other wood constituents. That is why the wood surface treatment is a highly demanding task. The coating materials applied on wood are exposed to degradation too; consequently, there are needed methods for enhancing wood protection effectiveness. The research in this area is mainly oriented on purpose-aimed surface modification of wood and coating materials planned for outdoor use when the system wood – solid coating is loaded more intensively than in indoor conditions.

The primary subjects of the current trends in this research area are: testing the stability of coatings containing nanoparticles, to coating materials modifying on organic-inorganic base, to 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, KÚDELA *et al*. 2016).

Compared to the outdoor exposure, wood products placed in indoor conditions are attacked by less intensive, but not negligible UV radiation. In addition, the demands on surface treatment quality in case of the products planned for indoor use (primarily furniture) are utmost strict. The surface treatment quality in furniture is assessed based on a set of chemical, physical, visual and mechanical properties as well as based on their appearance defects (KÚDELA 2012). The forefront parts of furniture are mainly judged according to their resistance against UV radiation effects and according their colour stability.

The aim of this work was to assess the colour changes on wood surface, generated in accelerated ageing process in indoor conditions. The wood surface was treated with commercially manufactured transparent coating materials. There was also tested influence of surface pre-treatment with a mordant dye.

MATERIALS AND METHODS

The test specimens were prepared from beech (*Fagus sylvatica* L.) wood. The basic set consisted of 45 specimens, each 100 × 50 ×10 mm (length × width × thickness) in size. The specimens were divided into nine groups, each consisting of five pieces. The specimens in the first group were left without surface treatment, the specimens of groups 2–5 were treated with the following four lacquers

- Duopur – polyurethane, polyester resin-based top coat, applied on the primer (without protective substance)
- PUR-One – yellowing, without protective agent,
- Ratiopur – non-yellowing, without protective agent,
- Ratiopur+ – non-yellowing, with protective agent against UV radiation.

The surfaces of specimens of groups 6–9 were, before lacquer applying, treated with a water-soluble mordent Aqua-Classic. This mordent contains special light-resistant, light-brown colorants. Then, the specimens were treated analogically as in groups 2–5.

Before the accelerated ageing, the colour of each specimen´s surface was measured and represented in a colorimetric space CIELab consisting of three orthogonal coordinates: L^* − coordinate expressing lightness, a^* − coordinate between red and green colour, b^* − coordinate between yellow and blue colour. There were carried 60 measurements in each above-specified group, by 12 on each specimen, at spots selected randomly and spaced uniformly across the specimen surface. The arithmetical means calculated from these values served us as reference colour values (variables indexed REF, Table 2). The measurements were performed with a spectre-photometer "Spectro-guide 45/0 gloss" (Fig. 1) by BYK-Gardner GmbH, performing within the wave range 400−700 nm.

The measurement of referenced values having finished, the specimens were placed into a Xenotest Q-SUN Xe-3-HS (Fig. 2) manufactured by Q-LAB, USA. The specimens were spaced uniformly and irradiated with three special UV lamps.

Fig. 1 Spectrophotometer Spectro-guide 45/0 gloss.

Fig. 2 Xenotest Q-SUN Xe-3-HS.

The ageing parameters in the xenotest followed the Standard ASTM G 155 and from paper KOLESKE *et al*. (1995). We selected the mode for outdoor conditions (so called „dry mode“) simulating conditions in which wood is exposed to radiation but protected from rain. The day light simulation in indoor conditions was provided with the aid of *Q-window Filters* situated under lamps. To guarantee the same values of radiation intensity and of temperature for all the specimens, the specimens were regularly and systematically moved about according to a schedule recommended.

Tab. 1 Ageing parameters set according to the Standard ASTM G 155.

Step	Mode	Radiation intensity (W/m²)	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

In accord with the Standard, the radiation intensity was set at 0.35 $W \cdot m^{-2}$ at a wave length of λ = 340 nm. This value corresponds to the mean annual value in the temperate zone. The temperature on a black panel represents the maximum temperature on the specimen surface. The air temperature was set to accelerate the changes generated on the wood surface. The radiation period was set to 100 h. After this time, the irradiation was interrupted and the colorimetric measurements on the specimen surface were performed again. Then the specimens were re-placed in the xenotest and irradiated for additional 100 hours. Finally, the colour measurements were repeated again (identical with the preceding measurements).

The objective colour response assessment was expressed through the colour differences ΔL^*, Δa^*, Δb^* and the total colour difference ΔE^* calculated according to the following equations

$$\Delta L^* = L_2 - L_1 \quad (1)$$

$$\Delta a^* = a_2 - a_1 \quad (2)$$

$$\Delta b^* = b_2 - b_1 \quad (3)$$

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (4)$$

where index 2 means the value after and the index 1 means the value before the wood surface ageing.

RESULTS AND DISCUSION

The results obtained by applying a three-way variance analysis suggest that the response in the colour space of the surface treated beech wood was significantly influenced by all the factors studied (coating material, mordant stained/unstained surface, ageing duration) as well as by their interactions.

The values of colour coordinates L^*, a^*, b^* of surface treated beech specimens measured before and after accelerated ageing process are summarised in Table2.

In case of specimens without mordant treatment, the table shows that compared to the native wood, there were certain changes to L^*, a^*, b^* coordinates after the surface treatment with the tested lacquers. All the tested lacquers enhanced to some extent the lightness of the specimens, with moderate drops in a^* coordinates, and moderate shifts in b^* coordinates towards yellow. The differences in the L^*, a^*, b^* coordinates values were also observed between the individual lacquers used for the surface finishing (Table 2).

In case of applying the mordant Aqua-Classic as a primer in advance of the finishing lacquer, there were generated considerable changes in L^*, a^*, b^* coordinates. Their grade responded to the hue of the colorant used.

Tab. 2 Measured values of L^*, a^*, b^* (before and after exposure) in Xenotest. The numeric index behind each variable represents the duration of exposure. (The values in parentheses represent standard deviation).

Colour space coordinate	Unstained surface					Stained surface			
	Native wood	Duopur	PUR-One	Ratiopur	Ratiopur+	Duopur	PUR-One	Ratiopur	Ratiopur+
L^*_{REF}	74,50 (23,77)	75.50 (2.88)	78.70 (0.72)	78.25 (1.46)	80.62 (0.71)	56.30 (0.74)	49.63 (0.66)	52.70 (0.56)	52.44 (0.83)
a^*_{REF}	6,78 (0,72)	5.93 (0.89)	5.82 (0.26)	6.22 (0.51)	5.30 (0.34)	20.17 (0.43)	22.72 (0.81)	22.15 (0.38)	22.98 (0.41)
b^*_{REF}	17,58 (0,78)	21.66 (2.33)	22.32 (0.41)	20.96 (0.67)	22.03 (0.61)	25.46 (0.68)	24.84 (0.94)	25.89 (0.57)	26.87 (0.39)
$L^*_{100\,h}$	66,52 (2,04)	64.20 (1.02)	66.05 (0.29)	65.88 (0.59)	72.03 (1.12)	51.90 (0.43)	50.56 (0.64)	52.00 (0.39)	50.02 (0.72)
$a^*_{100\,h}$	9,21 (0,55)	11.98 (0.38)	11.88 (0.15)	12.11 (0.23)	9.21 (0.57)	19.13 (0.14)	21.91 (0.39)	21.55 (0.21)	22.14 (0.31)
$b^*_{100\,h}$	26,48 (1,17)	29.34 (0.58)	31.42 (0.31)	31.39 (0.45)	22.11 (0.39)	26.20 (0.25)	28.53 (0.45)	29.94 (0.26)	24.90 (0.25)
$L^*_{200\,h}$	66,44 (2,04)	63.97 (0.77)	66.08 (0.45)	65.50 (0.68)	74.08 (0.97)	52.74 (0.72)	53.82 (0.59)	55.15 (0.53)	51.93 (0.86)
$a^*_{200\,h}$	9,65 (0,53)	12.67 (0.32)	11.82 (0.19)	12.25 (0.41)	7.77 (0.46)	18.78 (0.21)	21.68 (0.37)	20.89 (0.35)	22.01 (0.47)
$b^*_{200\,h}$	27,51 (1,31)	32.10 (0.49)	33.14 (0.40)	33.22 (0.57)	23.57 (0.44)	27.94 (0.41)	31.85 (0.47)	33.16 (0.40)	26.47 (0.37)

The colour changes on the wood surface were quantified through colour differences (Equations 1-4). All the values were calculated in relation to the reference ones measured before exposing the specimens to the radiation. Figs 3 and 4 display colour differences after 100h radiation exposure, Figs 5 and 6 illustrate the colour changes resulting from 200h exposure.

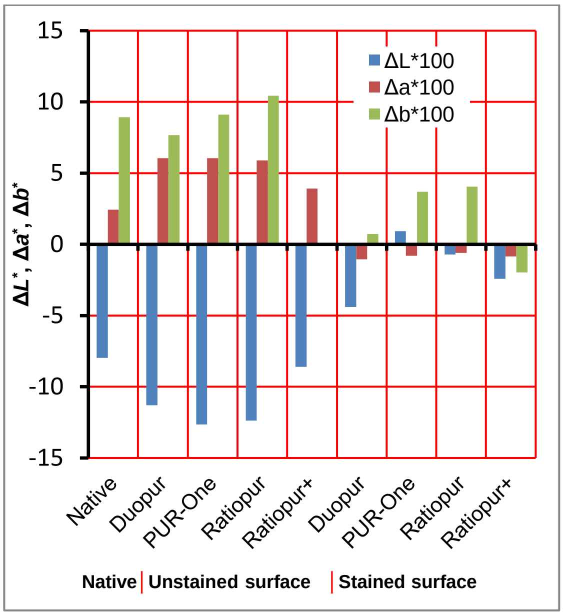

Fig. 3 Colour differences after 100 hours of accelerated ageing.

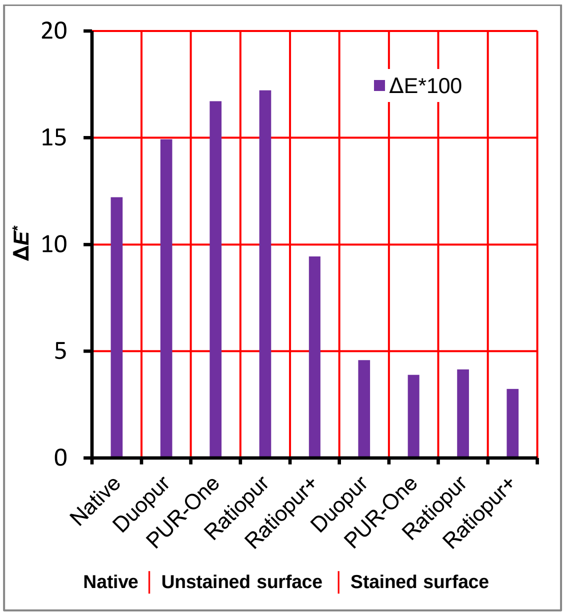

Fig. 4 Total colour differences after 100 hours of accelerated ageing.

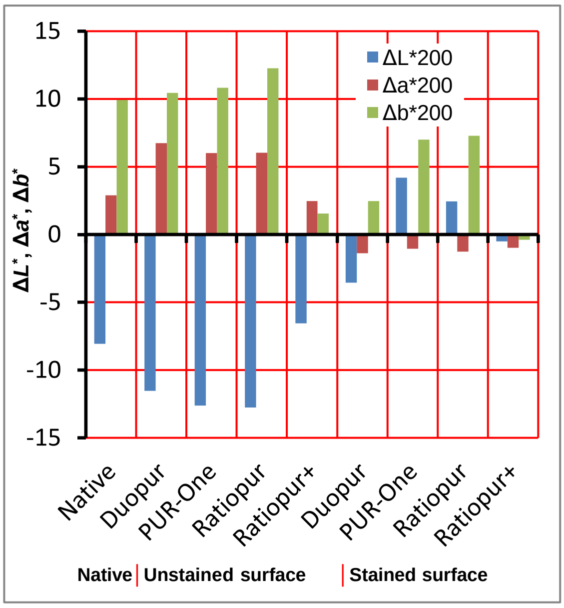

Fig. 5 Colour differences after 200 hours of accelerating ageing.

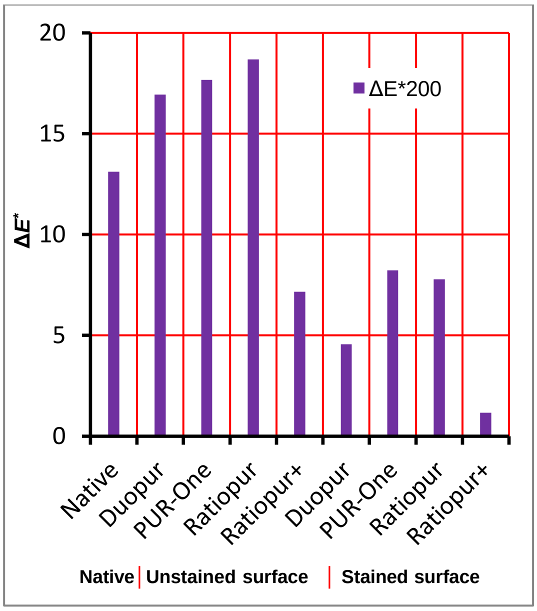

Fig. 6 Total colour differences after 200 hours of accelerating ageing.

In all cases, major colour changes were mostly generated after 100h exposure to radiation. All the specimens exhibited darker surface, with the exception of those pre-treated with the mordant and topped with the PUR-One and Ratiopur lacquers. The colour difference Δa^* meaning a shift towards red was increased in all specimens without mordant treatment. On the other hand, mordant-pre-treated surfaces displayed moderate drops in Δa^*, irrespective the lacquer type. Simultaneous shift to yellow was confirmed with the values on axis b^*, all higher, save the surface treated with mordant and finished with the lacquer Ratiopur+ (containing UV protection additives). Bigger increase in Δb^* was observed on samples without mordant pre-treatment than on those mordant-treated. On the surface without mordent, the total colour difference ΔE^* increased from the native, followed by Duopur, Pur-One, to Ratiopur. In all cases, the ΔE^* values were bigger than 12, which indicates that the surface colour after 100h accelerated ageing can be considered different form the original surface colour (colour difference degree 6). The surface topped with the lacquer Ratiopur+ displayed ΔE^* value considerably lower compared to the previous treatments ($\Delta E^* < 10$). Nevertheless, this is still classified as a considerable colour change (colour difference degree 5).

The colour changes associated with ageing process were more obvious on the surfaces treated with the lacquers Duopur, Pur-One, Ratiopur than on the native wood. This allows us to conclude; in accordance with OLLSON *et al*. (2014), that photodegradation in case of these surface treatments, was present in the wood as well as in the coating material. Our results, however, are not sufficient to specify unambiguously the proportions in which the coating and the wood participated.

The corresponding changes in coordinates L^*, a^*, b^* for mordant-treated surfaces topped with the same lacquers were considerably smaller (Fig. 3). Nearly four-time smaller was also the total colour change ΔE^* on mordant-treated surfaces finished with Duopur, Pur-One, Ratiopur in comparison with mordant-free surfaces coated with the same lacquers (Fig. 4).

Also in the case of mordant-treated surfaces, the best colour stability was found in the specimens treated with the lacquer Ratiopur+. In comparison with Ratiopur+ , the total colour difference ΔE^* on the mordant-free surfaces was three times smaller. The colour difference in all mordant-treated specimens was between the degrees 3–4 (colour difference visible with using a medium quality or a high-quality filter). Colour changes generated by ageing in the xenotest are also visualised in Figs 7 and 8.

Table 2 together with Figs 5 and 6 show that the impact of the second 100h ageing period in the xenotest was much weaker than the first 100h period. The lightness the mordant-treated specimens was without more significant changes. Equally, the Δa^* values were found without effectual change. On the other hand, there were significant changes in Δb^* due to the additional shift of the b^*coordinate towards yellow. After 200h ageing, the best colour stability was displayed by the mordant-treated specimens topped with Ratiopur+. In this case, the colour difference related to the same specimens before ageing was classified by the degree 2 meaning a small colour difference.

The experimental results revealed that the major colour changes occurred after 100h ageing. This fact is in accordance with LANDRY and BLANCHETT (2012), WAN *et al*. (2014) and others.

The results also show that the protection filter used in the case of Ratiopur+ had a considerable retarding impact on photo-degradation of the surface treated with this lacquer. Consequently, to prevent photo-degradation of furniture outer faces, these are needed to cover with coatings containing additives protecting against UV radiation.

Beech wood surface pre-treated, before applying the finishing lacquers, with the mordant Aqua-Classic manufactured based on special light-resistant colorants displayed considerably improved resistance against photo-degradation. The works REINPRECHT and PÁNEK (2015), KÚDELA *et al*. (2016) demonstrate also importance of the mordant hue and its hiding power.

The results obtained with ageing of mordant-treated surfaces revealed that the mordants generally used for homogenising the substrate colour and for mimicking outlook of exotic and precious wood species are effective in wood surface protection against UV radiation. From this viewpoint, it is useful to pre-treat wood with an appropriate mordent and subsequently to apply the specific lacquer.

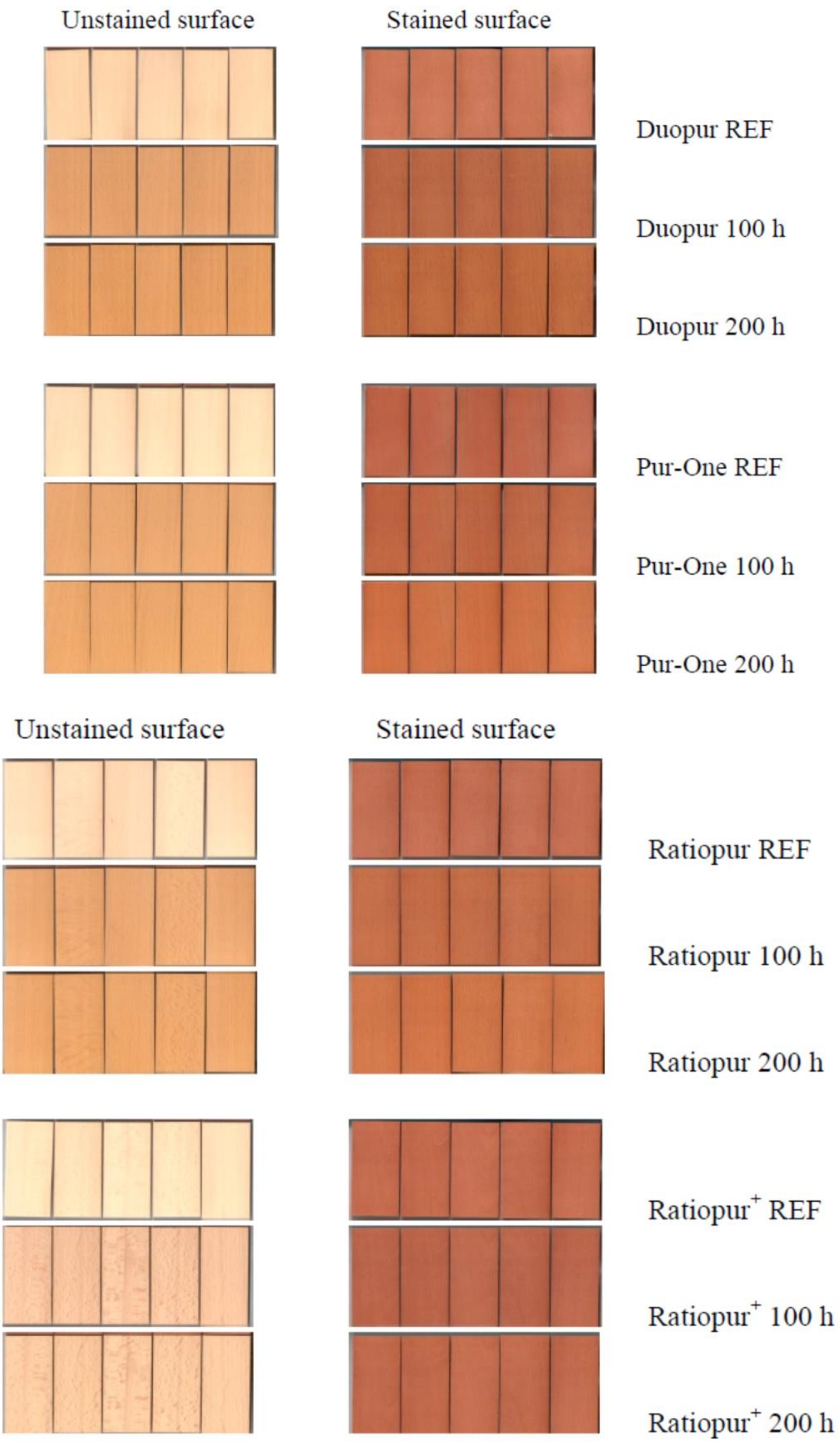

Fig. 7 Specimens colour before and after the accelerated ageing process.

CONCLUSION

Experimental testing of colour stability of beech wood surface treated with four lacquer types intended for surface treatment of wood products planned for interior use induced the following conclusion.

UV-induced photo-degradation of wood products surface-treated with lacquers takes place also in indoor conditions.

The measured and calculated colour change values demonstrated that the most colour changes are generated during the first 100 hours of accelerated ageing process.

The lacquer types were different in their capacity to protect wood surface against UV radiation effects. The lacquers without protective additives against UV radiation applied on beech wood could not inhibit its photo-degradation. Contrarily, the colour changes were even more pronounced than in the case of native beech wood. This was due to the photo-degradation of the coating material as well as of the wood surface.

Protective agents against UV radiation added into coating materials had important retarding effects on photo-degradation of the surface-treated wood.

Positive impact on colour stability of surface-treated wood was also found for its pre-treatment with a mordant manufactured based on special light-resistant colorants.

The best colour stability was found in the specimens pre-treated with the mordant and topped with the lacquer containing UV filter.

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