VERSITA DOI: 10.2478/v10303-012-0012-5 Acta Silv. Lign. Hung., Vol. 8 (2012) 145–155

Photodegradation of Timber of Three Hardwood Species Caused by Different Light Sources

László TOLVAJ* – Dénes VARGA

Institute of Physics and Electrotechnics, University of West Hungary, Sopron, Hungary

Abstract – In this study, resistance of black locust, beech and poplar wood to photodegradation was tested, applying sunlight, a xenon lamp and a mercury vapour lamp. The irradiation time was 200 hours for sunlight and the xenon light and 20 hours for the mercury light. The changes were monitored by colour measurements and infrared spectroscopy. The colour change of black locust was more intensive at the beginning of the irradiation than that of the beech and poplar. The degradation of aromatic structure of lignin (absorbing at 1510 and 1596 cm^{-1}) in black locust was minor compared to the same changes of beech and poplar during the first 10 hours. The mercury lamp induced more intensive changes both in colour and in infrared spectrum than the other two light sources. The results show that the high extractive content of black locust absorbs a considerable amount of light radiation protecting the main chemical components of wood.

colour change / infrared spectrum / mercury lamp / photodegradation / xenon lamp / wood

Kivonat – Három lombos fafaj faanyaga fotodegradációs tulajdonságainak összehasonlítása különböző fényforrások alkalmazása esetén. Akác, bükk és nyár faanyagok fotodegradációval szembeni ellenálló képességét vizsgáltuk napsugárzás, xenon lámpás és higanygőz lámpás besugárzás esetén. A kezelési idő 200 óra volt a napsugárzásos és a xenon lámpás besugárzásnál, és 20 óra a higanygőz lámpás besugárzásnál. A változásokat színméréssel és az infravörös spektrum felvételével követtük nyomon. A kezelés kezdetén az akác színváltozása sokkal intenzívebb volt, mint a bükké és a nyáré. Az első 10 órában a lignin aromás gyűrűjének degradációja (abszorpciós helyei: 1510 és 1596 cm^{-1}) akác esetében sokkal kisebb volt, mint bükk és nyár esetében. A higanygőz lámpás kezelés sokkal intenzívebb változást produkált (a színváltozásban és az infravörös spektrumban is), mint a másik két fényforrás. Az eredmények azt mutatják, hogy az akác magas extraktanyag tartalma elnyeli a fénysugarak jelentős részét, ezzel megvédve a faanyag fő kémiai összetevőit.

színváltozás / infravörös színkép / higanygőz lámpa /fotodegradáció /xenon lámpa / faanyag

1 INTRODUCTION

The colour inhomogeneity of wood is one of the most beautiful creations of nature. The colour hue of wood varies between red and yellow ensuring a warm and pleasant effect. This colour harmony of wood is however sensitive to light and heat. The combination of light and

* Corresponding author: tolla@fmk.nyme.hu; H-9400 SOPRON, Bajcsy Zs. u. 4.

heat treatment results in an even more intensive discoloration than separately (Mitsui et al. 2001, Mitsui 2004, Mitsui et al. 2004, Mitsui – Tsutchikawa 2005, Mitsui et al. 2005). The colour change of wood is the most sensitive indicator for the degradation caused by sunlight. The colour alteration of black locust wood can be seen after 2–3 hours of irradiation by the naked eye. The objective colour monitoring of photodegradation has been applied in wood science only for the last twenty years (Tolvaj – Faix 1995, Kawamura et al. 1996, Pastore et al. 2004, Pandey 2005, Oltean et al. 2009). For this purpose, the CIE L^* a^* b^* colour co-ordinate system has been used in most cases.

Sunlight is the main factor that causes the greatest changes in the surface properties of wood during outdoor exposure. Careful investigation of this type of degradation of wood is difficult with outdoor exposure because weather conditions are neither controllable nor repeatable. Therefore the light-induced degradation of wood is usually investigated under artificial conditions. The most frequently used artificial light source is a xenon lamp. As the ozone layer in the Earth's stratosphere is constantly dwindling, nowadays more ultraviolet (UV) radiation reaches the Earth's surface than before. Therefore the UV B wavelength region (280-315 nm) has to be taken into consideration. Xenon lamps have no emission in the UV B region while the emission spectrum of a mercury lamp has wider range of UV light (Tolvaj – Mitsui 2005).

Comparative studies on the effect of sunlight and artificial light sources in the weathering of wood can hardly be found in the literature. Ota et al. (1997) tested the colour stability of acetylated veneers of kiri (*Paulownia tomentosa* Steud.) irradiated by sunlight and light generated by mercury lamp. Podgorski et al. (1996) measured the effect of outdoor and artificial weathering of coated wood by glass transition temperature. The maximum value of glass transition temperature was found to be about 24°C. The cycles of treatment consisted of plunging samples into distilled water, drying and light irradiation with UV lamps. Pandey and Vuorinen (2008) carried out a detailed study of photodegradation of wood surfaces using a xenon lamp and a UV laser emitting at 244 nm. The UV resonance Raman spectra of laser irradiated wood showed similar behaviour as the wood irradiated by xenon light, i.e. overall broadening and a rapid reduction in the intensity of the lignin aromatic structure. The degradation rate caused by laser was very high. However, the extent of band broadening was higher in wood irradiated by xenon light indicating the generation of several different types of structures as compared to laser irradiation which produced only one type of structure.

Black locust wood has a high extractive content. This feature determines its high resistance to fungal attacks (Molnár – Bariska 2002), Pandey (2005) compared to the photo-discoloration of natural and extractive free wood samples. The extractive free specimens exhibited a monotonous increase in colour change with increasing irradiation time. Unextracted wood surfaces showed a rapid colour change during the initial period of exposure which decreased after a prolonged exposure time. Analysis of colour changes and FTIR spectra measured on irradiated wood surfaces indicate that the presence of extractives increases the rate of photo-discoloration and results in an apparent increase of the delignification rate of wood surfaces in the initial period of exposure. The apparently increased rate of delignification in unextracted wood has been explained on the basis of photo-degradation of polyphenolic extractives.

In our experiments, the samples were exposed to sunlight only on sunny days to determine the effect of sunlight alone. The objective of this work was to compare the photodegradation effects of black locust, beech and poplar wood caused by natural and two different artificial light sources. Another aim of this study was to find a test method which can simulate the changes in wood surface discolouration caused by sunlight.

2 MATERIALS AND METHODS

The investigated hardwood species were: black locust (*Robinia pseudoacacia*), beech (*Fagus crenata*) and poplar (*Populus canescens*). The species were chosen because of the differences in extractive content. Black locust has a high extractive content (4–9%) while poplar has hardly any extractives. Black locust is often used in outdoor applications. Poplar species are sometimes used as structural wood. Beech has medium extractive content and it often shows unwanted discolouration in furniture due to sunlight, even in indoor use. Planed surfaces with a tangential orientation were prepared. The tangential surface was chosen to reduce the colour inhomogeneity of the surface. The sample size was 50x10x2 mm^3. The samples of different series were prepared from the same board. All species were represented by a series of 2 samples, and 5 points of fixed location were measured. The data presented in this work are the average of 10 measurements. The absolute value of the data is not important for these investigations. Since only the tendency of change is important, no statistical analysis was made. No deviations were found in tendencies of changes for the two samples. The number of replicates is not relevant because the aim was to find whether the artificial light sources can imitate the effect of sunlight. The measurement of 5 independent points is enough to represent the colour data of a wood sample (Németh 1981).

One natural and two artificial irradiation types were chosen to be able to compare the effect of sunlight to the effect of the regularly applied artificial light sources. The natural sunlight irradiation was carried out between 5th of May and 19th of August, 2003 (air temp. varied 16-41 °C, max. r.h. 80% and the daily average of total solar power density was between 436-459 W/m^2) in Takayama (Gifu Prefecture, Japan). Geographical data for Takayama are: 36 degrees 9.3 minutes latitude and the altitude was 560 meters. The samples were exposed outside only on sunny days to determine the effect of the sunlight alone. After exposure the samples were stored in total darkness in the laboratory. The other series of specimens were irradiated with a soft irradiation source, a xenon lamp at 180 W/m^2, in the range of 300–400 nm, at 63 °C (black panel) and 50% r.h., in a commercial chamber (SX-75: Suga Test Instruments Co. Ltd., Tokyo). There was a quartz glass filter around the lamp. Unfortunately, the xenon lamp emits less UV radiation than sunlight. That is why a strong UV light emitter, a mercury vapour lamp also was used to irradiate specimens (HAL 800NL, installed into a KBP.659 Nippon Denchi Co. Ltd. chamber). The total light emission of the mercury lamp was 320 W, and the samples were located 64 cm from the lamp. The air temperature in the chamber was 26 °C. The emission spectrum of the mercury lamp contains 31% UV-A (380–315 nm), 24% UV-B (315–280 nm) and 25% UV-C (>280 nm) radiation. The total irradiation time was 200 hours for sunlight and the xenon light, and 20 hours for the mercury light. The irradiation with a mercury lamp produces much greater changes than the other two types of irradiation. That is why the irradiation was stopped after 20 hours.

The colour of the wood specimens was measured before and after irradiation. The exposures were interrupted after 5; 10; 20; 30; 60 and 120 hours (for the mercury lamp these data were ten times smaller) to measure the colour data. The colour measurements were carried out with a colorimeter (SE-2000 Nippon Denshoku Industries Co. Ltd., Tokyo). The *L**, *a**, *b** colour co-ordinates were calculated based on the D65 light source. The infrared (IR) spectra measurements were made with a JASCO FTIR double beam spectrometer equipped with a diffuse reflectance unit (JASCO: DR-81). The resolution was 4 cm^{-1} and 64 scans were obtained and averaged. The background spectrum was obtained against an aluminium plate. The spectral intensities were calculated in Kubelka-Munk (K-M) units. The spectra were normalised to the band between 1350 cm^{-1} and 1405 cm^{-1}, and a two point baseline correction at 3800 cm^{-1} and 1900 cm^{-1} was carried out.

3 RESULT AND DISCUSSION

The colour of wood is mainly determined by its extractives. Thus the colour change originates mostly in the chemical changes of the extractives. The degradation of the main components (cellulose, hemicelluloses and lignin) of wood can be monitored by IR spectroscopy. However the chemical changes of extractives cannot be followed by IR spectroscopy because they are present in a relatively low concentration. The IR spectrum of wood is rather complex because of its complicated chemical structure. The calculation of the difference spectrum (the spectrum after irradiation minus the bulk spectrum) is often used for presenting the changes. In this case only those bands are visible which showed alterations. *Figure 1* presents the difference IR spectrum "fingerprint region" of black locust created by 200 hours of irradiation by sunlight. After irradiation, the carbonyl band between 1680 and 1850 cm^{-1} increased and the peak of the aromatic skeletal vibration originating from lignin at 1596 and 1510 cm^{-1} decreased together with the guaiacyl vibrations at 1275 cm^{-1} as noted in previous studies (Horn et al. 1994, Pandey – Theagarayan 1997, Kosikova – Tolvaj 1998, Ohkoshi 2002, Müller et al. 2003, Sudiyani et al. 2003, Mitsui – Tsuchikawa 2005). Usually, two peaks develop in the 1680–1850 cm^{-1} region during the exposure of wood to UV radiation. It was strengthened by 2D IR correlation spectroscopy (Popescu et al. 2011). The splitting of the ether bands is also visible at 1171 and 1138 cm^{-1} wavenumber.

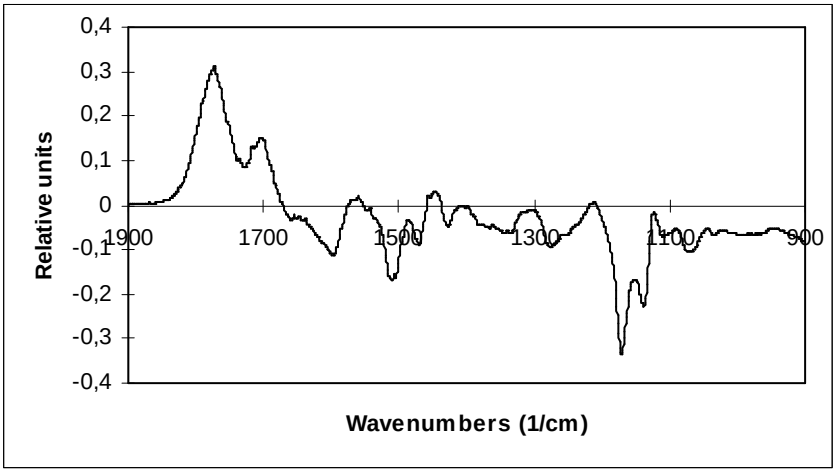

Figure 1. Difference IR spectrum of black locust after 200 hours irradiation by sunlight

The degradation of lignin is demonstrated by the decrease of IR bands at 1596 and 1510 cm^{-1}. This is presented in *Figure 2*. These data were created by sunlight irradiation.

The trend lines in *Figure 2* are parallel. The only difference is that lignin molecules of black locust which absorb at 1510 cm^{-1} did not undergo changes during the first 10 hours of irradiation. This phenomenon shows the protecting effect of extractives at the beginning of the irradiation. This period was shorter than 10 hours for the artificial light sources. If the extractives have already degraded, the protection of lignin breaks down. This is presented by the parallel trend lines. The lignin of unprotected poplar suffered the greatest degradation in all cases. The greatest absorption decrease of poplar was 0.34 units at 1510 cm^{-1}. It was generated by a mercury lamp during 20 hours of irradiation. The decrease of the absorption at 1596 cm^{-1} was similar but smaller than the decrease of the absorption at 1510 cm^{-1}.

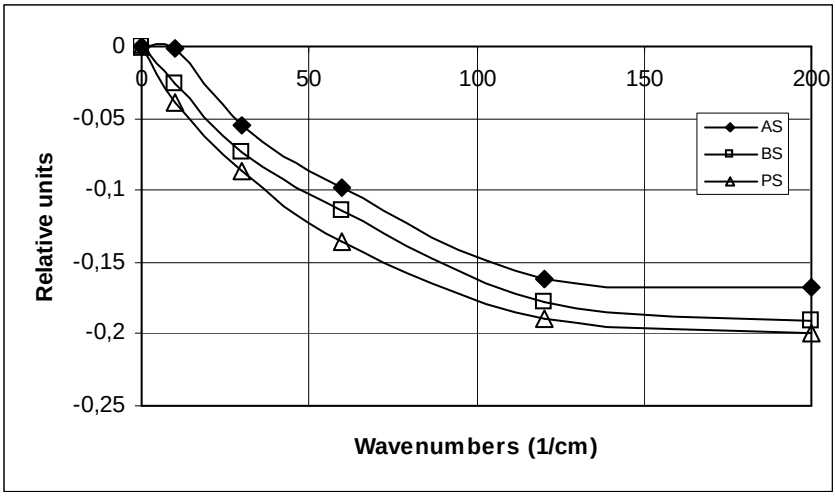

Figure 2. IR absorption change of aromatic ring for lignin at 1510 cm^{-1} produced by sunlight irradiation (for abbreviations see Fig. 7)

The natural colour of wood is beautiful but at the same time it is extremely sensitive to light radiation. UV light in particular causes remarkable colour changes. Colour change is more pronounced initially during exposure than the other indicators. In some species, this colour change is notable and visible to the unaided eye after only a few hours of radiation. During the first 20 hours of light irradiation by sun or a xenon lamp, the lightness change was rapid as shown in *Figure 3* and *Figure 4*. The rapid period of bleaching caused by sunlight contributed 76% to the total change in black locust, 58% in beech and 39% in poplar. The extraordinary behaviour of black locust can be explained by its high extractive content. The UV light degrades the extractives followed by the rapid oxidation of the degradation products. This is presented by the rapid lightness decrease. The modified chromophores act as a kind of energy trap which slow down the photodegradation of the main wood components (Németh et al. 1992).

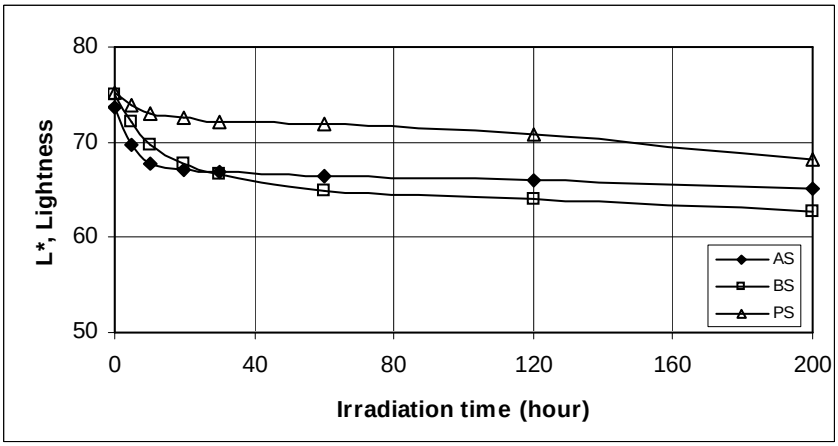

Figure 3. Lightness change of black locust (A), beech (B) and poplar (P) samples caused by sunlight (S)

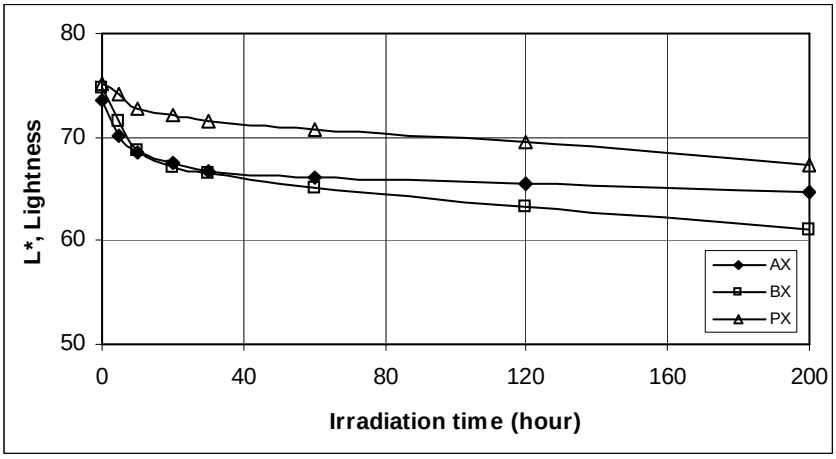

Figure 4. Lightness change of black locust (A), beech (B) and poplar (P) samples caused by a xenon lamp (X)

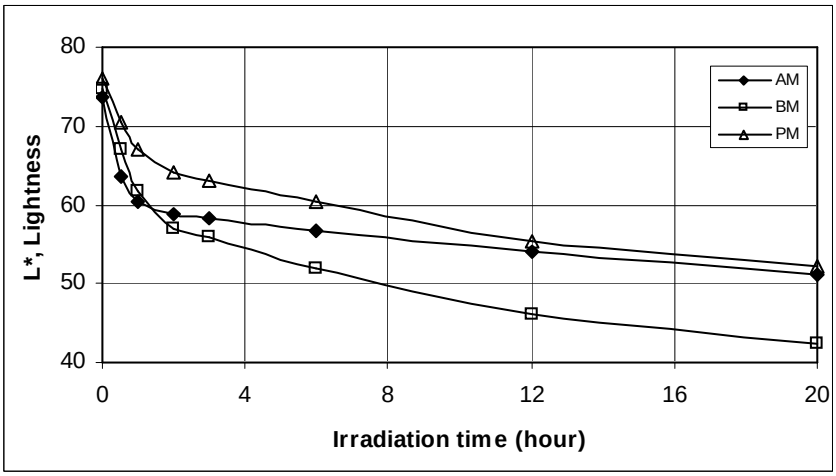

Figure 5. Lightness change of black locust (A), beech (B) and poplar (P) samples caused by a mercury lamp (M)

This effect is thought to be the main reason for the slower lightness change of black locust after 20 hours of irradiation compared to other examined species. It is well visible in *Figures 3–5*. The xenon lamp created a slightly greater change than sunlight. The effect of the mercury lamp irradiation (*Figure 5*) differs from that caused by a xenon lamp or natural exposure. The decrease of lightness was intensive in the whole examined time period. The mercury light irradiation was applied for up to 20 hours. This is 10 times shorter than for the other two light sources. Considering this period, the tendencies of changes were similar as it is visible comparing *Figures 3*, *4* and *5*. The mercury lamp caused more intensive colour changes than the other two light sources because the emission spectrum of the mercury lamp is mainly in the UV region (80%).

Comparing the decreasing tendency of lightness caused by the three light sources (*Figures 3–5*), we conclude that the behaviour of black locust is different to that of the other two species irrespective of the light source. Poplar samples produced the smallest lightness change. The rapid decrease in the first 10% of irradiation time is missing because poplar wood hardly has any extractives. Therefore poplar is a good reference to determine the effect of extractives. Beech has high extractive content; however the main extractives of beech and black locust are chemically different. Extractives of beech provide less protection against photodegradation compared to the extractives of black locust.

The change of red hue (*a**) presents even more deviation of black locust compared to the other two wood species (*Figures 6–8*). Only the strong UV light emitting mercury lamp produced similar changes (*Figure 8*) in all cases. The red hue shift of black locust was extremely fast during the first 5 hours of treatment. This increase represents 59% of the total increase of *a** during the xenon lamp irradiation. At the same time, the red hue shift of poplar and beech was slight. In the second period of the treatment (after 60 hours), the red hue of black locust hardly changed, while that of the other two species increased continuously. The xenon lamp induced a greater red hue shift than sunlight during the first 80 hours of exposure. The tendency of the changes was highly different at the beginning of the irradiation. The most intensive change of red colour was created by the mercury lamp irradiation.

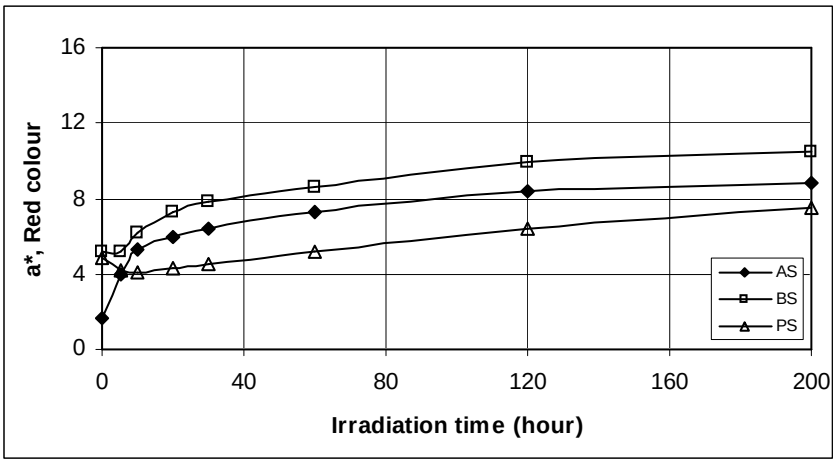

Figure 6. Red hue shift of black locust (A), beech (B) and poplar (P) samples caused by sunlight (S)

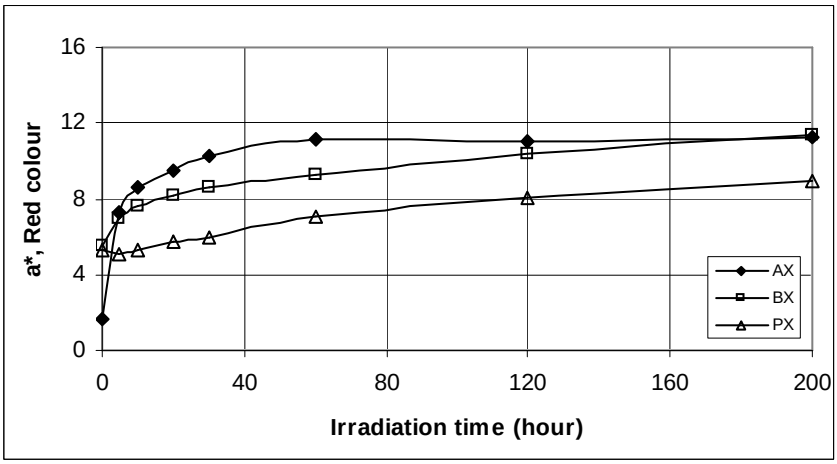

Figure 7. Red hue shift of black locust (A), beech (B) and poplar (P) samples caused by a xenon lamp (X)

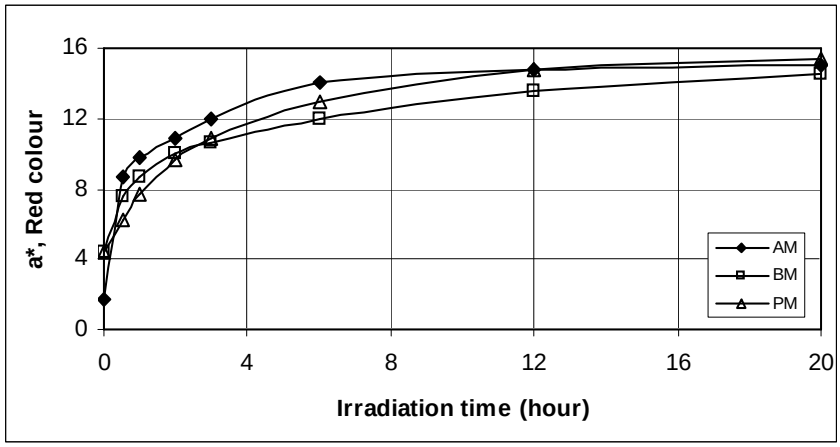

Figure 8. Red hue shift of black locust (A), beech (B) and poplar (P) samples caused by a mercury lamp (M)

The yellow hue of the samples increased continuously during the irradiation (*Figures 9–11*). As the initial yellow colour (*b**) of black locust is higher than that of the other two species, the trend line of black locust is located above the others. The only exception is in *Figure 11* where the low extractive content of poplar was unable to protect the lignin against the strong UV radiation of the mercury lamp. The degradation products of lignin created the increase of yellow colour. This observation is verified by the IR data (*Figure 2*). The xenon lamp induced a greater yellow shift than sunlight during the first 40 hours of exposure. The tendency of the changes was highly different at the beginning of the irradiation.

All three colour co-ordinates demonstrate that the photodegradation properties of black locust are more accentuated compared to the same properties of poplar. The extractives of black locust samples suffered rapid degradation at the beginning of the light irradiation. The degradation products partly protected the surface of the samples during further light irradiation. In contrast, poplar suffers continuous degradation during irradiation since it has no extractives to protect the surface.

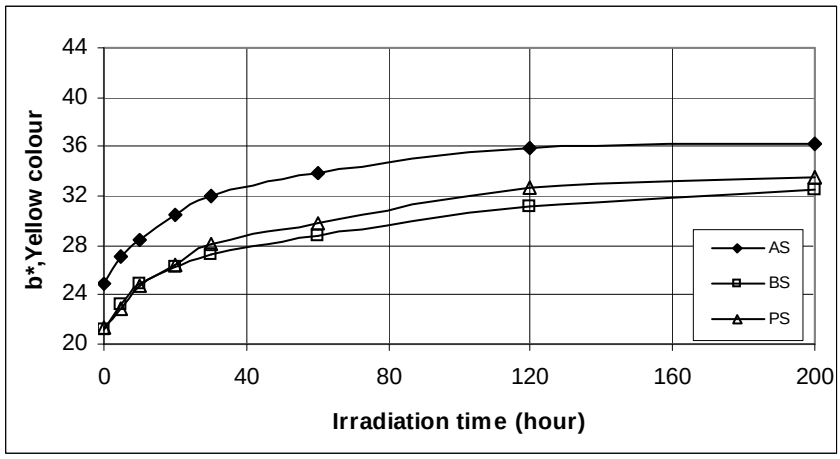

Figure 9. Yellow hue shift of black locust (A), beech (B) and poplar (P) samples caused by sunlight (S)

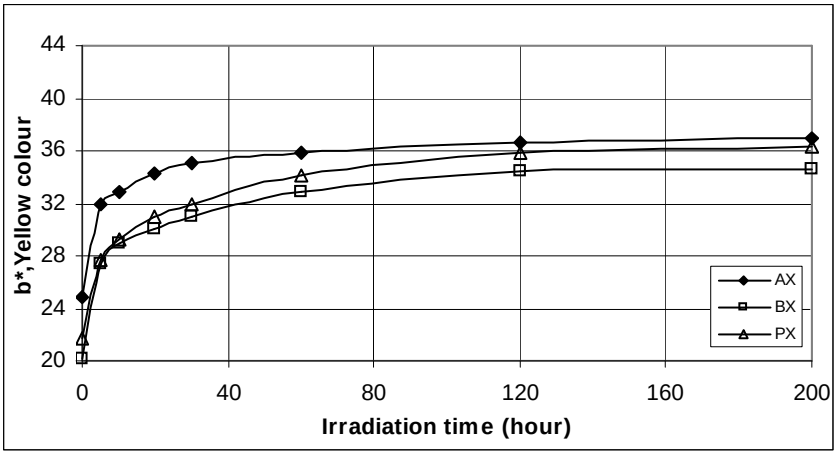

Figure 10. Yellow hue shift of black locust (A), beech (B) and poplar (P) samples caused by a xenon lamp (X)

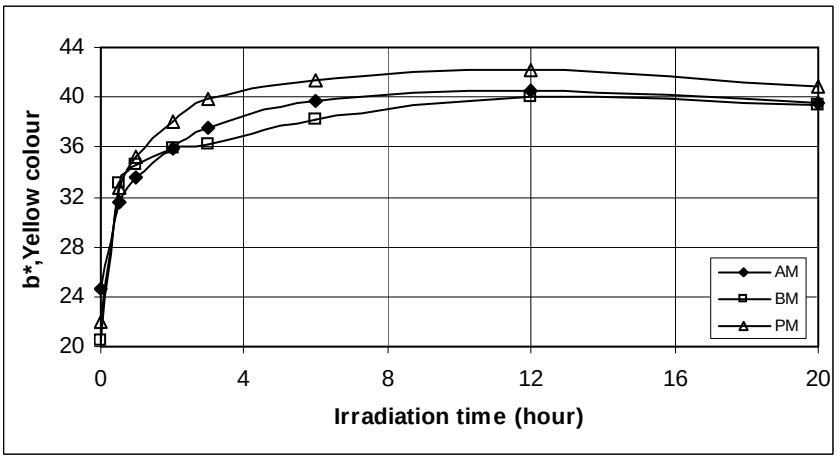

Figure 11. Yellow hue shift of black locust (A), beech (B) and poplar (P) samples caused by a mercury lamp (M)

4 CONCLUSIONS

The colour change of black locust was more intensive at the beginning of the irradiation than that of the beech and poplar. The degradation of the aromatic structure of lignin (absorbing at 1510 and 1596 cm^{-1}) in black locust was minor compared to the same changes of beech and poplar during the first 10 hours. These results show that the extractives of black locust are highly sensitive to light irradiation. These extractives suffered rapid degradation at the first period of the light irradiation. Lightness change, red and yellow hue shifts of black locust revealed that the degradation products protect other extractives and partly protect the lignin. This protection was confirmed by the changes of the IR spectra. The IR spectra of the investigated species showed that poplar is the most exposed because of its lack of extractives. Xenon light is able to simulate the effect of sunlight during weathering only after long exposure times. In the short term, the changes of red and yellow hues are faster and greater from xenon light irradiation compared to sunlight. The mercury lamp as a strong UV emitter is suitable to study photodegradation but unable to simulate the effect of sunlight.

REFERENCES

HORN, B.A. – QIU, J. – OWE, N.L. – FEIST, W.C. (1994): FT-IR Studies of weathering effects in western redcedar and southern pine. Appl. Spectrosc. 48: 662–668

KAWAMURA, F. – OHASHI, H. – KAWAI, S. – TERATANI, F. – KAI, Y. (1996): Photodiscoloration of Western Hemlock (*Tsuga hterophilla*) Sapwood I. Actual conditions upon photodiscoloration of wood parts. Mokuzai Gakkaishi 42 (3): 293–300

KOSIKOVA, B. – TOLVAJ, L. (1998): Structural changes of lignin- polysaccharide complex during photodegradation of Populus grandis. Drevarski Vyskum 43: 37–46

MITSUI, K. – TAKADA, H. – SUGIYAMA, M. – HASEGAVA, R. (2001): Changes in the properties of light-irradiated wood with heat treatment. part 1. effect of treatment conditions on the change in color. Holzforschung 55 (6): 601–605

MITSUI, K. (2004): Changes in the properties of light-irradiated wood with heat treatment. Part 2. Effect of light-irradiation time and wavelength. Holz Roh Werkstoff 62: 23–30

MITSUI, K. – MURATA, A. – TSUCHIKAWA, S. – KOHARA, M. (2004): Wood photography using light irradiation and heat treatment. Color Res. Appl. 29 (4): 312–316

MITSUI, K. – TSUCHIKAWA, S. (2005): Low atmospheric temperature dependence on photodegradation of wood. J. Photochem. Photobiol. B: Biol. 81: 84–88

MITSUI, K. – TOLVAJ, L. – PAPP, G. – BOHUS, J. – SZATMÁRI, S. – BERKESI, O. (2005): Changes in the properties of light-irradiated wood with heat treatment. Part 4. Application of laser. Wood Research 50 (1): 1–8

MOLNÁR, S. – BARISKA, M. (2002): Wood species of Hungary. Szaktudás Kiadó Ház, Budapest, 54–60

MÜLLER, U. – RÄTZSCH, M. – SCHWANNINGER, M. – STEINER, M. – ZÖBL, H. (2003): Yellowing and IR-changes of spruce wood as result of UV-irradiation. J. Photochem. Photobiol. B: Biol. 69: 97–105

NÉMETH, K. (1981): Színmérés a faiparban I. A természetes fa színmeghatározása [Colour measurement in wood industry I. Colour determination for natural wood.] Faipar 31 (9): 257–261

NÉMETH, K. – VANÓ, V. – FAIX, O. (1992): The effect of wood extractives on the photodegradation of wood. EWLP Conf. Grenoble, France. 191–192

OHKOSHI, M.J. (2002): FTIR-PAS study of light-induced changes in the surface of acetylated or polyethylene glycol-impregnated wood. J. Wood Sci. 48: 394–401

OLTEAN, L. – HANSMANN, C. – NÉMETH, R. – TEISCHINGER, A. (2010): Wood surface discolouration of three hungarian hardwood species due to simulated indoor sunlight exposure. Wood Research 55(1):49–58

OTA, M. – OGATA, H. – JONO, Y. – HIROTA, K. – ABE K. (1997): Light-induced color changes of acetylated veneers of kiri (Paulowniatomentosa Steud.). Mokuzai Gakkaishi 43: 785–791

PANDEY, K.K. – THEAGARAJAN, K.S. (1997): Analysis of wood surfaces and ground wood by diffuse reflectance (DRIFT) and photoacustic (PAS) Fourier transform infrared spectroscopic techniques. Holz Roh Werkstoff 55: 383–390

PANDEY, K.K. (2005): A note on the influence of extractives on the photo-discoloration and photo-degradation of wood. Polym. Degrad. Stab. 87 (2):375–379

PANDEY, K.K. (2005): Study of the effect of photo-irradiation on the surface chemistry of wood. Polym. Degrad. Stab. 90(1): 9–20

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 (12): 2138–2146

PASTORE, T.C.M. – SANTOS, K.O. – RUBIM, J.C. (2004): A spectrocolorimetric study on the effect of ultraviolet irradiation of four tropical hardwoods. Bioresource Technol. 93 (1): 37–42

PODGORSKI, L. – MERLIN, A. – DEGLISE, X. (1996): Analysis of the natural and artificial weathering of a wood coating by measurement of the glass transition temperature. Holzforschung 50: 282–287

POPESCU, C.M. – POPESCU, M.C. – VASILE, C. (2011): Structural analysis of photodegraded lime wood by means of FT-IR and 2D IR correlation spectroscopy. Int. J. Biol. Macromolecules 48: 667–675

SUDIYANI, Y. – IMAMURA, Y. – DOI, S. – YAMAUCHI, S. (2003): Infrared spectroscopic investigations of weathering effects on the surface of tropical wood. J. Wood Sci. 49: 86–92

TOLVAJ, L. – FAIX, O. (1995): Artifical ageing of wood monitored by drift spectroscopy and cie l*a*b* color measurements. i. effect of uv light. Holzforschung 49 (5): 397–404

TOLVAJ, L. – MITSUI, K. (2005): Light source dependence of the photodegradation of wood. J. Wood Sci. 51 (5): 468–473