Research paper

Effects of Simulated Sunlight on the Photodegradation of Untreated and Copper (II) Ethanolamine-treated Wood

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【Summary】

A series of experiments was carried out to investigate the effect of simulated sunlight on the photodegradation of untreated and copper (II) ethanolamine-treated Norway spruce wood (*Picea abies* (L.) Karst). For this, 1 set of wood samples was vacuum-pressure-impregnated with an ethanolamine aqueous solution, while the other set of samples was taken as an untreated control sample. Both the untreated and treated wood samples were intermittently exposed to artificial sunlight for 500 h. Color measurements were carried out throughout the irradiation period at intervals of 100 h according to the CIE L*a*b* system. Better color stability was recorded for treated wood, compared to untreated wood. The electron paramagnetic resonance and diffused reflectance infrared fourier transform spectroscopic tests showed that the better photostability of treated wood during artificial sunlight irradiation resulted from modifications of lignin and monomers of phenolic compounds.

Key words: Norway spruce wood, photodegradation, artificial sunlight, EPR spectroscopy, DRIFT spectroscopy.

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研究報告

銅(II)乙醇胺處理材與未處理材
照射模擬太陽光之光劣化效應

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摘　要

　　本系列試驗係進行評估銅(II)乙醇胺處理之挪威雲杉(*Picea abies* (L.) Karst)與未處理材照射模擬太陽光之光劣化效應。基於此目的，一組木材樣品是依真空一加壓一注入程序，注入銅(II)乙醇胺水溶液，然而另一組樣品是未處理的對照組。未處理和處理之木材樣品二者是間歇性的曝露在人工太陽光下共500 h，整個照射期間每隔100 h依CIE L*a*b*系統執行顏色測量。結果顯示，經處理之木材比未處理者具有更好的顏色穩定性。從電子順磁共振(electron paramagnetic resonance)和擴散反射霍氏轉換紅外線光譜(diffused reflectance irfrared fourier transform spectroscopic)分析顯示，經處理之木材於人工太陽光照射下引發木質素改質和形成酚類化合物單體，而導致較佳的光穩定性。
關鍵詞：挪威雲杉、光劣化作用、人工太陽光、電子順磁共振光譜、擴散反射霍氏轉換紅外線光譜。

INTRODUCTION

Wood is a 3-dimensional polymeric composite, made up chiefly of cellulose, hemicellulose, and lignin. If natural wood is exposed to sunlight, it initially leads to a fast color change due to absorption of electromagnetic radiation, and at further stages, it leads to large chemical alterations and a breakdown of the wood surface layer (Ayadi et al. 2003). This complex breakdown process in combination with exposure to precipitation, often described as weathering, plays an important role in using wood as outdoor constructional materials (George et al. 2005, Hansmann et al. 2006). The color stability of natural wood to light exposure is an important issue from an esthetics point of view. With exposure to light, some woods become bleached or gray, whereas others turn yellow, reddish-orange, or brown, depending on the influence of their extractive compositions (Hon 2001, Kamdem and Grelier 2002).

The ultraviolet (UV) spectrum of sunlight is one of the most effective among all environmental factors that contribute to the weathering process of wood (Futo 1974, Ayadi et al. 2003). Although the UV spectrum represents only 5% of the energy in sunlight, its strong effects on wood's degradation processes are well documented (Hon 2001). Mostly, the UV spectrum absorbed by light-irradiated wood initiates photochemical reactions that ultimately may lead to wood discoloration and photodegradation (Hon 2001, George et al. 2005). Photodegradation also results in an increase in cellulose and a decrease in lignin concentration on the wood surface layer (Evans et al. 1992, George et al. 2005), and it ultimately leads to the deterioration of physical, chemical, and biological properties of natural wood.

Absorption of light by lignin leads to the formation of free radical species (presumably phenoxyl radicals) with long lifetimes (Lin and Kringstad 1970, Hon and Feist 1981, Hon 1994, Petric et al. 2004). These free radicals react with oxygen to produce carbonyl and carboxyl chromophoric groups (Hon and Feist 1992), which are responsible for wood color changes (Ayadi et al. 2003). It is well established that apart from sunlight and temperature, oxygen plays an important role in the photodegradation processes of wood. Water is also considered to be a critical element in wood's photodegradation processes (Feist et al. 1991, Hon 2001, Hansmann et al. 2006).

To limit the photodegradation of wood, coatings as well as chemical and thermal modification processes have been attempted (Tomazic 2006, Petric et al. 2007, Deka and Petric 2008). Unlike coatings, a modification process is a 1-time treatment for the entire service-life of the wood (Rowell et al. 1981, Williams 1983, Kamdem and Grelier 2002). The color stabilization of natural wood to be used in decorative end-uses like parquet, panels, furniture, etc. is required. Although, acetylation inhibits wood yellowing, it causes lightening upon exposure to sunlight. Treatment of wood with water-soluble inorganic salts of chromium, iron, and copper was reported to protect the wood surface from photodegradation to some extent (Williams and Feist 1988, Evans et al. 1994, Liu et al. 1994, Humar et al. 2003, Petric et al. 2004). However, the toxicity of chromium salt solutions limits their application in wood-modification processes (Ayadi et al. 2003, Humar et al. 2004). Due to higher costs, the grafting of polyethylene glycol and hydroxylphenyl-benzo-triazole onto wood surfaces with isocyanate groups is not economical, although these chemicals were found to be effective against wood surface discoloration (Ayadi et

al. 2003). Therefore, the search for new modification processes to stabilize wood surfaces to color change would easily find important industrial applications.

In our present experiment, surface color stabilization of copper ethanolamine-treated spruce wood during artificial sunlight exposure was studied and compared to untreated wood. For our present experiment, a copper (II) ethanolamine (CuEA) system was selected to treat the wood, because it is an emerging preservative for the future due to its non-toxicity, unlike arsenic and chromium preservatives (Kamdem and Grelier 2002, Humar et al. 2003, Humar et al. 2004, Petric et al. 2004). Since, the treatment process in our experiment has industrial applicability, we stressed the importance of evaluating its performance for surface color stabilization during simulated solar irradiation.

MATERIALS AND METHODS

Wood material

Eight rectangular blocks of spruce (*Picea abies* (L.) Karst) wood were cut from a single air-dried log to ensure homogeneity. Then, 12 test samples of $50 \times 10 \times 50$ mm (radial $\times$ tangential $\times$ longitudinal) were prepared from each block. The samples were then placed in a climate chamber at 25℃ and 50% relative humidity to stabilize the weight prior to treatment. The moisture content of the test samples after exposure to climate chamber was 12%.

Treatment of the samples

The wood samples made from each of the blocks were divided into 2 sets. By means of an industrially relevant process, 1 set was impregnated with a water-borne copper preservative, while another set was used as untreated, as a control. For copper impregnation,

an (alkaline pH 9.8) aqueous solution of copper ethanolamine (with a concentration of Cu of 0.5% and of EA of 2.9% in mol) was used. The molar ratio of copper and ethanolamine was 1:6. The samples were impregnated under a vacuum (-0.09 MPa), high pressure (0.6 MPa), and normal pressure in sequence for 40 min each. The impregnation of the wood samples resulted in a solution uptake of about 400 kg m^{-3}. Later, the samples were conditioned for 4 wk, the first 2 wk in closed chambers, the third week in half-closed, and the fourth week in open ones. After treatment, all samples were conditioned in the climate chamber as mentioned above prior to artificial sunlight light irradiation.

Artificial sunlight irradiation

One-half of each of the treated and untreated wood samples was irradiated with an Osram Ultra-Vitalux 300 W sunlamp (Ljubljana, Slovenia) at a distance of 50 cm. The biological effect of this lamp after 1 h of irradiation was approximately 6~7-times greater than that of normal sunlight with UVA (315~400 nm) and UVB (280~315 nm) radiation levels of 13.6 and 3 W, respectively. The samples were irradiated for 500 h intermittently with a 1-wk break after each 100 h of exposure to evaluate their properties. Thus, the values of different properties evaluated in our experiment were the average of 24 parallel measurements.

Color measurement

The color of light-irradiated surfaces of the test samples was measured with an X-Rite SP Series Spectrophotometer (X-Rite In. S.W. Grandville, MI, USA). The reflection spectrum was acquired from a measuring spot of 20 mm in the 390~710 nm region; whereas at least 3 measurements at precisely defined spots on the irradiated surface of each of the

samples were carried out after an interval of 100 h throughout the entire experimental period. The color changes due to light irradiation were monitored with the help of L*a*b* color spaces before and after exposure to light as per the CIE (Commission Internationale de 1'Eclairage) L*a*b* system. Then, overall color differences, ΔE*, were computed using the following expression (Brock et al. 2000).

$$\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}; \qquad (1)$$

where, ΔL*, Δa*, and Δb* are changes between the initial and final values of L*, a*, and b*, respectively.

Electron paramagnetic resonance (EPR) measurement

EPR spectra were recorded at room temperature using a Bruker (Ljubljana, Slovenia) ESP-300 X-band spectrometer (with a microwave frequency of 9.62 GHz, a microwave power of 20 mV, a modulation frequency of 100 kHz, and modulation amplitude of 0.1 mT). Two matchstick-like samples ($30 \times 1 \times 1$ mm) were cut from each sample and inserted into the resonator, 1 at a time. Intensities of the free-radical signals were measured from the amplitude of the free-radical signal and were normalized with respect to the mass of the sample. Since, the line-width of the free-radical signal was the same for all wood samples, the amplitude of the signal corresponded well with the amount of free-radicals in the wood (Schmid et al. 2000).

Diffused reflectance infrared Fourier transform (DRIFT) spectroscopy

Using Abrasive Pad 600 Grit-Coated, PK/100 (Perkin-Elmer, Grandville, Michigan, USA) paper, DRIFT spectra of irradiated surfaces of treated and untreated wood samples were recorded between 4000 and 450 cm^{-1} with a Perkin-Elmer FTIR Spectrum One spectrometer. The reflectance spectra obtained

were then transformed into Kubelka-Munk units as a function of the wave number averaged over 16 scans.

RESULTS AND DISCUSSION

Assessment of the treatment procedures (impregnation with CuEA) is shown in Table 1, and it is clear that treated wood substrates had a quite-different darker color than untreated wood. The color changes of treated and untreated wood due to artificial UV light irradiation for different time periods are presented in Fig. 1. It is clear from the figure that both treated and untreated wood samples showed rapid color changes during the first 100 h of exposure to light. More than 70% of the color changes were observed during the first 200 h of irradiation for all substrate types. However, a higher discoloration rate was observed in the case of untreated wood samples from the beginning with pronounced separation from the treated wood samples. Discoloration of untreated wood always exceeded that of treated wood throughout the entire experimental period.

Untreated wood

The overall color changes (ΔE^*) for un-

treated wood increased from 0 to 24.1 after 500 h of exposure to light compared to CuEA-treated wood, for which this value changed from 0 to 13.3 (Table 1, Fig. 1). The value of ΔE^* recorded for untreated wood was around 2-times higher than that of CuEA-treated wood. The higher color changes as a result of artificial light irradiation for untreated wood was due to the higher contribution of the chromaticity coordinates, Δa^*, Δb^*, and ΔL^* (Table 1). The negative value of ΔL^* for untreated wood, indicates that light-irradiation darkened the wood surface. The darkening of light-irradiated surfaces of untreated wood might have been due to degradation of lignin and other non-cellulosic polysaccharides
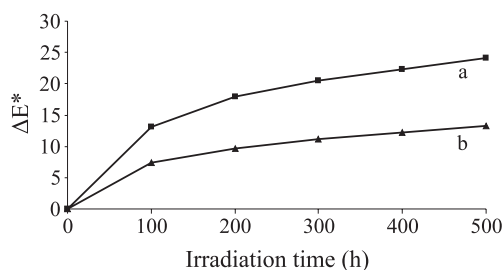

Fig. 1. Color changes (ΔE^*) of untreated (a) and CuEA-treated (b) spruce wood during UV light irradiation for different time periods.

Table 1. Influence of treatment (impregnation with CuEA) on the color of spruce wood and color changes of treated and untreated spruce wood after artificial UV light irradiation for 500 h

Influence studied	Color components[1]			
	ΔE^*	ΔL^*	Δa^*	Δb^*
Un-irradiated CuEA-treated				
CuEA	33.1 (1.7)[2]	-32.2 (1.5)	-3.3 (0.3)	8.4 (0.6)
Irradiated, substrate type				
Untreated	24.1 (0.8)	-11.9 (0.7)	7.8 (0.4)	19.5 (0.6)
CuEA treated	13.3 (0.9)	0.03 (0.6)	5.6 (0.3)	12.1 (0.9)

[1] Values in parenthesis are standard deviations.

[2] Relatively high standard deviation values are the consequence of the fact that assessment of color differences due to treatment procedure was not based on measurements on exactly the same blocks or even spots but just on very similar (regarding orientation and texture) samples.

(Grelier et al. 2000, Petric et al. 2004). The increase in the chromaticity coordinates, Δa^* and Δb^* by 7.8 and 19.5, respectively, for untreated wood indicated yellowing and reddishness due to exposure to light. This can be attributed to the formation of quinones and quinone-like structures resulting from depolymerization and oxidation of lignin involving free radicals (presumably, phenoxyl radicals) in this process (Kamdem and Grelier 2002, Ayadi et al. 2003). The involvement of free-radical reactions in color changes of exposed surfaces was proven by the observed increase in free-radical signals in the EPR spectra of untreated wood after exposure to light (Fig. 2). Chemical changes occurring in untreated wood during light exposure, which ultimately resulted in color changes, were also detected by IR spectroscopy. Figure 3 shows the chemical changes of untreated wood surfaces due to light irradiation. A weak band in the case of light-irradiated samples compared to non-irradiated samples at about 2900 cm^{-1} was due to methylene-CH_2 stretching in lignin and xylan, and benzene ring vibrations in lignin. It is also apparent from the IR spectra that light-irradiated wood surfaces showed decreases in absorption bands at 1508 and 1264

cm^{-1}, which are due to benzene ring stretching vibrations and -C=O group stretching vibrations in lignin, respectively (Harrington et al. 1964). The weak decrease in absorption bands at these wavelengths reveals degradation (loss) of lignin (Ohkoshi 2002, Petric et al. 2004), thereby causing color changes in irradiated wood. Likewise, a weak band in the case of light-irradiated samples compared to non-irradiated samples at 1451 cm^{-1} was due to -CH_2 deformation vibrations in lignin and xylan, and benzene ring vibrations in lignin. Strengthening of the band at around 1725 cm^{-1} for irradiated wood can be attributed to the formation of non-conjugated carbonyl groups and degradation of lignin that ultimately resulted in surface color changes (Ohkoshi 2002). The light-irradiated samples also showed a reduction in intensity of the absorption band at around 806 cm^{-1}, which might have been due to degradation of non-cellulosic polysaccharides and hemicelluloses (Harrington et al. 1964).

CuEA-treated wood

The value of color changes (ΔE^*) of CuEA-treated wood due to artificial light irradiation for 500 h was around 45% less than
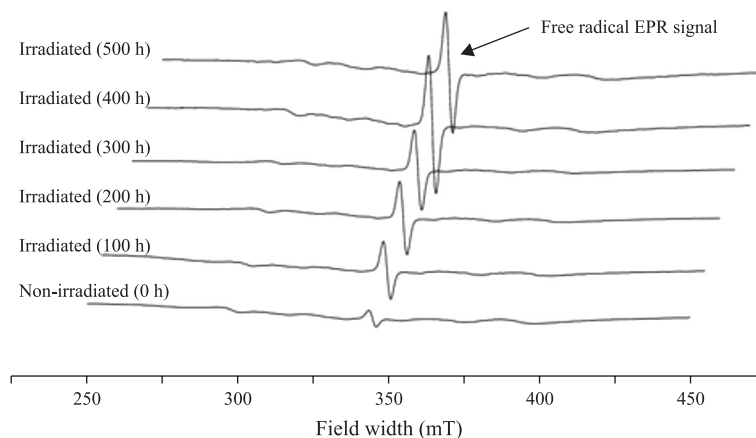

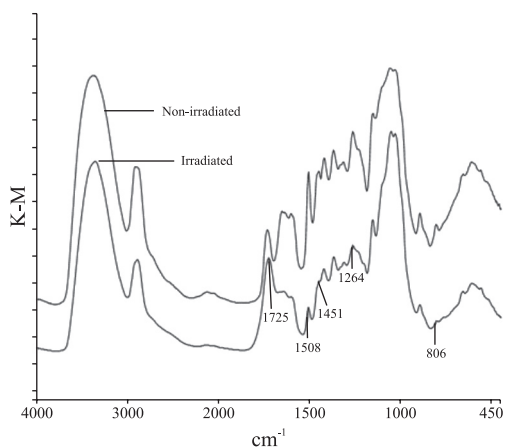**Fig. 2. EPR spectra of untreated spruce wood after irradiation with artificial UV light for different time periods.**

Fig. 3. Infrared spectra of untreated spruce wood after 0 and 500 h of irradiation to artificial UV light.

Fig. 4. Infrared spectra of CuEA-treated spruce wood after 0 and 500 h of irradiation with artificial UV light.

the value for untreated wood (Table 1). This indicates the efficacy of the CuEA formulation used for wood protection in our present experiment against photodegradation. Previously, a similar result was recorded for Cu-amine-treated wood (Liu et al. 1994). However, as in a previous study (Grelier et al. 2000), the surface color of CuEA-treated wood in our experiment changed from bluish-green to grayish-brown after light exposure as a result of copper retention during treatment. That the CuEA took part in the process of color stability of treated wood, compared to untreated wood, can be well argued with the help of IR spectroscopic data (Fig. 4). A decrease in the absorption band in the case of light-irradiated samples (for both treated and untreated) compared to non-irradiated samples at about 2900 cm^{-1} was due to methylene-CH_2 stretching in lignin and xylan, and benzene ring vibrations in lignin. The decrease in the absorption band at this wavelength reveals degradation (loss) of lignin (Petric et al. 2004), thereby causing color changes in irradiated wood. The absorption band of the IR spectra (Fig. 4) at 1733 cm^{-1} was primarily believed to be
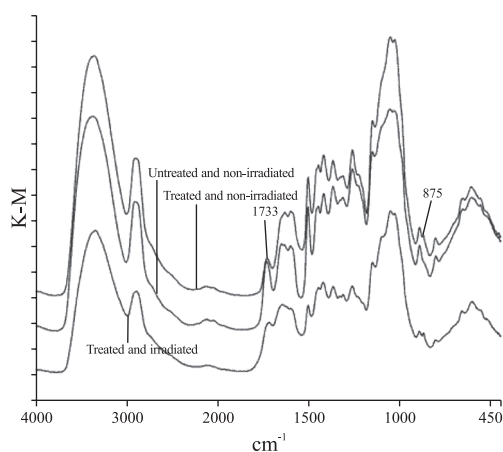
due to -C=O stretching vibrations of carboxyl and acetyl groups in xylane (Harrington et al. 1964). The weakening of this absorption band in case of CuEA-treated wood compared to untreated wood might have been due to a reaction between ethanolamine and -C=O groups in xylane as reported by Petric et al. (2004). The absorption band of treated wood at around 875 cm^{-1} might have been due to the influence on benzene ring deformation vibrations because of the chemical reaction with ethanolamine. However, the IR spectra of light-irradiated wood samples did not show any remarkable difference with non-irradiated ones (Fig. 4), which indicates the efficacy of CuEA treatment against photodegradation.

The contributions of the chromaticity coordinates, Δa^*, Δb^*, and ΔL^*, to overall color changes of CuEA-treated wood during light irradiation were found to be much lower than those of untreated wood (Table 1). This reveals that CuEA formed complexes with wood components, and in turn, these complexes limited the formation of substances with chromophoric groups, for which color stability was achieved compared to untreated

wood. The interaction of CuEA with phenolic groups of lignin forms a phenolate, which retards the formation of phenoxy radicals involved in color changes (Kamdem and Grelier 2002). In our present study, this was proven, as EPR spectra showed no free-radical signals even after 500 h of exposure to light for CuEA-treated wood (Fig. 5). In Fig. 5, only the typical Cu(II) EPR signals in Cu-treated wood can be seen (Humar et al. 2004). Photo-oxidation and photodegradation processes of organic substrates in homogeneous and heterogeneous systems within the generalized Cu(II)-Cu(I) photocatalytic redox cycle were thoroughly reviewed and presented by Sykora (1997). It was shown by numerous examples, mainly from an environmental point of view, that Cu(II) may be photo-reduced into Cu(I). This reaction is reversible. Hydrogen peroxide and various free-radicals (e.g., hydroxyl, superoxide ions, etc.) are involved in the process. The photoinduced Cu(II)-Cu(I) cycle in fact, like reactions of the catalytic system, which consists of copper, hydroperoxides, and copper coordination compounds that contain aromatic nitrogen atoms, is similar to those of catalytic centers of oxidative en-

zymes involved in delignification reactions of white rot fungi (Fackler et al. 2000). They demonstrated that 1-electron transfers from the substrates to the reactive intermediate of the copper/pyridine/hydrogen peroxide reaction, presumably a copper-oxo or copper-peroxo species occur. Schmid et al. (2000) studied the photostabilizing effects of copper-containing wood preservatives by means of EPR spectroscopy. They believed that certain copper-based wood preservatives could reduce the concentration of free radicals formed when treated wood was exposed to UV light. To prove this hypothesis, they treated a number of thin Scots pine veneers with 2 different copper-containing wood preservatives and placed them in an EPR spectrometer, which allowed the samples to be exposed to UV radiation while the spectra were recorded. The results showed a smaller concentration of free radicals in preservative-treated veneers than in untreated controls. Their hypothesis was that a transfer of electrons from the organic radicals to copper occurred. Similarly, Kamdem and Grelier (2002) hypothesised that the presence of copper in wood could cause the destruction of hydroperoxide species and,
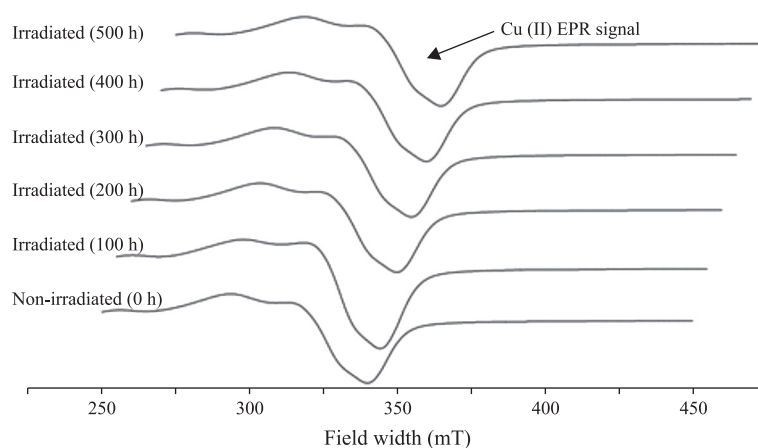

Fig. 5. EPR spectra of CuEA-treated spruce wood after irradiation with artificial UV light for different time periods.

therefore, decrease photodegradation.

The hypothesis of electron transfer from various free-radical species was extensively studied by Krzisnik (2001). His EPR study of copper preservative-impregnated and UV-irradiated thin spruce wood slices showed a decrease of free-radical signal intensities compared to intensities in untreated wood. At the same time, a decrease in the Cu(II) EPR signal was noted. Krzisnik (2001) suggested that the observed Cu(II) signal decrease supported the theory of the Cu(II) to Cu(I) conversion, i.e., electrons being delivered by transfer from free-radical species. Therefore, we strongly believe that our results support the data mentioned in the literature. However, we think that free radicals formed during UV irradiation in our experiment were trapped by copper (II) in the wood, and therefore, photostabilized them. For that reason, they could not be resolved on the EPR spectra. However, in terms of this theory, the question of why we did not observe a decrease in the Cu(II) signal in our EPR spectra arises. We think that the concentration of copper in the impregnated wood was relatively high, while on the other hand, the concentration of free radicals formed during photodegradation of the wood and the reaction with Cu(II) was rather small. So, presumably a small decrease of Cu(II) line intensities could not be detected on broad and strong Cu(II) EPR signals. Tattini et al. (2004) showed that substances like flavonoids could screen UV wavelengths. Temiz et al. (2005) assumed that wood-ion complexes formed with copper at the wood surfaces provide resistance to wood surfaces to photodegradation by blocking the free phenolic groups, which are the reactive sites of photochemical reactions. The complex between Cu(II) and non-substituted curcumin was shown to exhibit sunscreen properties (Sundayono et al. 2003). Taking into account

those data, one may think that apart from a radical-scavenger mechanism of wood protection against photodegradation by Cu(II), another possible photo-protective mechanism in CuEA-treated wood could be screening of UV light by various Cu(II) complexes in our test specimens.

CONCLUSIONS

CuEA treatment was found to be effective in photostabilization of wood in terms of color stabilization during long-term artificial sunlight light exposure. The photostabilization of wood by CuEA treatment might have been due to a reaction of CuEA with phenolic groups of lignin to form a phenolate, which retards formation of phenoxy radicals which cause color changes.

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