COLOUR CHANGES IN WOOD SURFACES MODIFIED BY A NANOPARTICULATE BASED TREATMENT

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ABSTRACT

This work reports on the colour changes in wood surfaces, namely from the species European pine, fir, Bosnian pine, chestnut and cherry, which have been modified by a new nanoparticulate treatment. Colour values (CIE L*, a*, b*) for both control and treated wood samples have been studied for each of the five different species. The results have shown a certain effectiveness of the anti-UV surface treatment used, while lower effects were due to ultraviolet light induced photodecolouration.

The largest improvements against discolouration were observed with cherry wood. It was observed that anti- UV compound applied on chestnut was particularly less effective (ΔL= -4.64) in respect to other species. It appears that the yellowness show systematic trends with anti-UV treated samples. However, the UV irridation appears to change surface yellowness of coniferous species more than hardwood species. The anti-UV treated hardwood surfaces (chestnut and cherry) yielded higher gloss than the anti-UV treated softwoods (pine and fir).

KEYWORDS**:** Wood, ultraviolet radiation, nanoparticulate based treatment, European pine (*Pinus sylvestris*), Bosnian pine (*Pinus leucodermis*), Greek fir (*Abies cephalonica*), chestnut (*Castanea sativa*), cherry (*Prunus avium*).

INTRODUCTION

Wood has been used for centuries for fuel and as a construction material. Typically it is an organic material, being composed of cellulose fibers embedded in a matrix of lignin and hemicelluloses. The main problems relating to aesthetic appearance of wood occur when exposed outdoors; unprotected wood is easily discoloured under athmospheric exposure (Sahin 2002). The discolouration is occasional and colour changes may vary. However, the abnormal discolouration of wood often denotes a diseased condition indicating unsoundness. Moreover, sapwood and heartwood of the same species undergo different types of photodecolouration (Mazet et al. 1993).

The ultraviolet (UV) light from sun is one of the biggest problems for the use of wood in the exterior environment. As it is known, light consists of very dense small particle bundles, which are called photons. However, the photons have certain wavelength (λ) and energy level (E). Sahin (2002) proposed that light with a wavenumber lower than 400 nm has enough energy to create new reactions on wood structure, thus causing a chemical bond to break.

The discolouration of wood is a serious aesthetical drawback, for example, in outdoor furniture and parquetry. However, UV protective agents are among the most important practices used in the wood industry. As compared to unprotected surfaces, the reason for using surface protective agents is trying to keep the colour of wood as natural as possible. Technological progress has been made with the development of new, anti-UV surface compounds, which offer significant benefits compared to currently used UV absorbers (Hayoz et al. 2003).

Although significant chemical differences exist between softwoods and hardwoods, especially as far as it concerns hemicelluloses and lignin (Fengel and Wegener 1984, Young 2008), however, it is known that the main wood chromophores are located on lignin, and 90–95% of the light absorption of wood can be ascribed to lignin (Hon 1991, Muller et al. 2003). The role of lignin in the photodegradation of wood was described by Feist and Hon (1984).

The UV degradation process is due to the formation of free radicals with the oxidation of phenolic hydroxyls (Hon 1991, Zahri et al. 2007, Rosu et al. 2010). Rosu et al. (2010) found that colour changes (Delta E-ab) correlate well with the formation of chromographic groups on wood surface and degradation of lignin. Zahri et al. (2007) found that discolouration of wood under UV exposure was mainly related to lignin and extractives content. They found that, in addition to lignin degradation, more than half of the phenolic content of extractives decreased after the UV exposure of wood. It was then proposed that the yellowing of lignocellulosic materials indicates the modification of lignin and holocellulose. Tolvaj and Mitsui (2010) reported that light irridated wood species showed a rapid colour change at the initial period of treatment, but the rate of change decreased with treatment time. Several researchers suggested that yellowing and/or brightness measurements are useful to characterise the photodegradation of lignocellulosic surfaces (Zahri et al. 2007, Yamamoto et al. 2007, Wang and Ren 2008, Tolvai and Mitsui 2010).

Wood discolouration can affect the natural appearance of wood species causing serious economic problems in the wood industry. Outdoor discolourations have been widely studied and are well understood. In addition, discolourations caused by sapstain and mould fungi can be industrially controlled. Conversely, UV irridated discolourations have received a rather lesser attention. Hence, our current study is investigating a new developed nanotechnology surface protecting agent and its effects on wood colour properties under UV irridation. Due to their small size, such nanoparticles based typically on some metal oxides, can deeply penetrate into wood, effectively altering its surface chemistry and resulting in higher protection against discolouration. Several research works relating to such nanotechnology compounds have been carried out recently (Cayton et al. 2010, Vlad Cristea et al. 2010, Beyer et al. 2010, Kaygin and Akgun 2008).

Hence, the aim of this work was to examine the influence of a new nanoparticulate surface treatment on several wood species, when exposed to UV radiation by measuring surface colour changes and parameters thereof.

MATERIAL AND METHODS

A new surface anti-UV agent based on a nanoparticulate compound was applied on air dry surfaces of European pine (*Pinus syslvestris*), Bosnian pine (*Pinus leucodermis*), Greek fir (*Abies cephalonica*), Chestnut (*Castenea sativa*) and Cherry (*Prunus avium*) wood samples; samples had been conditioned to 12% moisture content prior to experiments. Eight samples from each species were cut in the form of 50 x 50 x 20 mm. Commercially available, a new anti-UV nanocompound named Hombitec RM 400 (Sachtleben, Germany) was applied to samples in athmospheric conditions, simply by soaking in a bath for 30 sec. After the treatment, both surface treated and untreated samples were conditioned to 12% moisture content in a conditioning room at 65% relative humidity and 20 ^{0}C for a week.

The UV irridation on wood samples was conducted in a UV chamber with single UVA-340 lamps. This irridation period was in total for 400 hours and specimens were exposed to the UV environment directly. The distance between the samples and the lamp during irradiation were 20 cm. Temperature within the irradiation chamber was about 25 ^{0}C.

The discolouration of wood specimens coated with UV resistant agent was determined using a colour spectrophotometer (X-Rite SP62 Portable Spectrophotometer). The device was calibrated against a white and black working standard supplied with the instrument. Measurements were made using a D65 illuminant and a 10-degree standard observer. The five measurements for each treatment conditons of the wood species were made and average colour values were calculated.

The CIE L*a*b* colour scale (Commission Internation de l'Eclairage, 1976) was used to quantify the changes on colour; where L* stands for lightness, a* stands for redness and b* stands for yellowness. The colour variables of surface layer of wood, and the difference in colour, ΔE_{ab}*, between them, were determined. ΔE_{ab}* was calculated as follows:

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

The improvement (%) of colour properties was calculated as;

Improvement (%) = 100*(A-B / A).

Where:
A= UV exposed untreated wood, B= treated and UV exposed wood

The gloss of wood specimens was determined according to ASTM D523 (1970) with a suitable measuring device (Pacific Scientific Galossgard II, 60 degree Glossmeter). Results were based on a specular gloss value of 100, which relates to the perfect condition under identical illuminating and viewing conditions of a highly polished, plane, black glass surface.

RESULTS AND DISCUSSION

The comparative surface colour properties of untreated woods that used in this study were summarized in Tab. 1. The cherry and chestnut wood substrate that are hardwoods, have Lightness (L) values of 69.48 and 68.42, green-red (a) values of 9.18 and 5.97, blue-yellow (b) values of 23.37 and 22.31, respectively. However, Bonian pine, European pine and Greek fir which are softwoods have Lightness (L) values of

71.1, 79.59 and 75.88, green-red (a) values of 9.3, 5.41 and 5.54, blue-yellow (b) values of 29.87, 23.54, and 26.26, respectively. With having these measured results, it is reasonably described that softwoods look like a lighter colour appearance.

(Table 1)

A comparative summary of the measured colour values (CIE L*, a*, b*) for both control and anti UV treated samples is shown in Table 2. It appears that type of wood species significantly influenced colour values. As expected, the anti-UV treatment significantly improved the lightness (ΔL), redness (Δa) and yellowness (Δb) of species. The highest lightness improvement (79.4%) was observed with cherry, followed by fir (52.9%), European pine (48.1%), Bosnian pine (10.6%) and chestnut (4.32%), respectively. It was observed that anti- UV compound applied on chestnut was particularly less effective (ΔL= -4.64) in respect to other species. On the contrary, the improvement in yellowness was the largest in chestnut (129.6%). Meanwhile, the highest redness (Δa) improvement (91.6%) was observed with cherry, followed by chestnut (57.8%), European pine (45.5%), fir (35.8%) and Bosnian pine (14.6%), respectively.

Yamamoto et al. (2007) has already reported that there was a tendency for initial colour of wood species and their discolouration patterns: the smaller the initial lightness value was, the darkening/bleaching transition occurred for L*; the larger the initial a* value was, the darkening/bleaching transition for a; and there was no obvious tendency for b*. However, the quantification of all colour variables is very complicated, not easy to interpret, because the discolouration of wood represents a phenomenological parameter, which is characterised by both anatomical and chemical interactions. But this observation however, clearly shows that this anti-UV compound treatment is quite effective in inhibiting the photo discolouration of wood.

(Table 2)

Mazet et al. (1993) proposed that the colour change of wood during photodegradation can be correlated with yellowness properties. Hence, for verifying surface yellowness changes of wood species under UV exposure, the surface yellowness properties (reported as index) of both control and anti-UV treated wood were estimated and shown in Table 3. It appears that all treatment conditions significantly influenced yellowness values. Untreated cherry and chestnut samples have characteristically high yellowness values of 26.64 and 20.13, respectively. However, the UV irradiation can act synergistically within the wood substrate. These effects fade of natural colour of substrate. The lowest yellowness value was determined for anti-UV treated samples of chestnut (0.45) and cherry (0.58). It was found out that the yellowness show systematic trends with anti-UV treated samples. However, the UV irradiation appears to change surface yellowness of coniferous species more than hardwood species.

(Table 3)

As described above, the used anti-UV surface treatment reduced photo discolouration induced by ultraviolet light. However, the total colour difference (ΔE) which in this study was used to determine the discolouration surface layer can be used so as to give an estimate on how colour change affects the natural colour of wood. In the literature, ΔE values of 2-3 are thought to be observable colour difference (Muller et al. 2003). As for the wood samples treated with this anti-UV compound, their ΔE values were all lower (Fig. 1). However, the differences are obviously more readily distinguished in light-colour softwoods than in dark-colour hardwood species. In general, the results of this study on the effect of UV irradiation on anti-UV treated wood surfaces are compatible with the findings in the literature (Vlad Cristea et al. 2010, Beyer et al. 2010).

Feist and Hon (1984) have showed that the rate and type of free radical formation heavily depends on the irradiation energy and therefore on the wavelength. Since, reaction mechanism in the wood-light system primarily depends on the chemical interactions between those; it is possible that increasing kinetic energy in wood-light system results in the discolouration of wood. However, at well bonded anti-UV compound and wood polymer constituents, discolouration is probably due to interaction of easily accessible cells regions of carbohydrates and lignin.

Fig. 1

To find out the extent of discolouration, surface colour properties further measured with a glossmeter. Fig. 2 shows the gloss properties of untreated and anti-UV treated samples that irridated with UV. The anti-UV treated hardwood surfaces (chestnut and cherry) yielded higher gloss than the anti-UV treated softwoods (pine and fir). This suggests that gloss and surface colour properties (CIE L*,a*,b*) are independent of each other, and that quantitation of discolouration in case of several wood species is very difficult. It has been well known that hardwoods usually have darker colour than softwoods. However, experimental results indicate more or less similar findings for hardwood species, which has a higher gloss loss and discolouration compared to softwoods (Tabs. 1 and 2).

Fig. 2

CONCLUSIONS

The colour changes in wood surfaces of European pine, fir, Bosnian pine, chestnut and cherry, which had been modified by a new nanoparticulate treatment were studied in here. The results have shown a certain effectiveness of the anti-UV surface treatment used; however it is necessary to employ some stabilizers to inhibit this discolouration for specific wood species, namely Bosnian pine.

However, wood discolouration appears to be a phenomenical issue and not well understood for most wood species. To determine the causes of discolouration one has to understand factors such as extractives composition, temperature, humidity, light and storage conditions. However, discolouration is merely an indication of a chemical modification, which does not itself affect all of the colour properties of wood.

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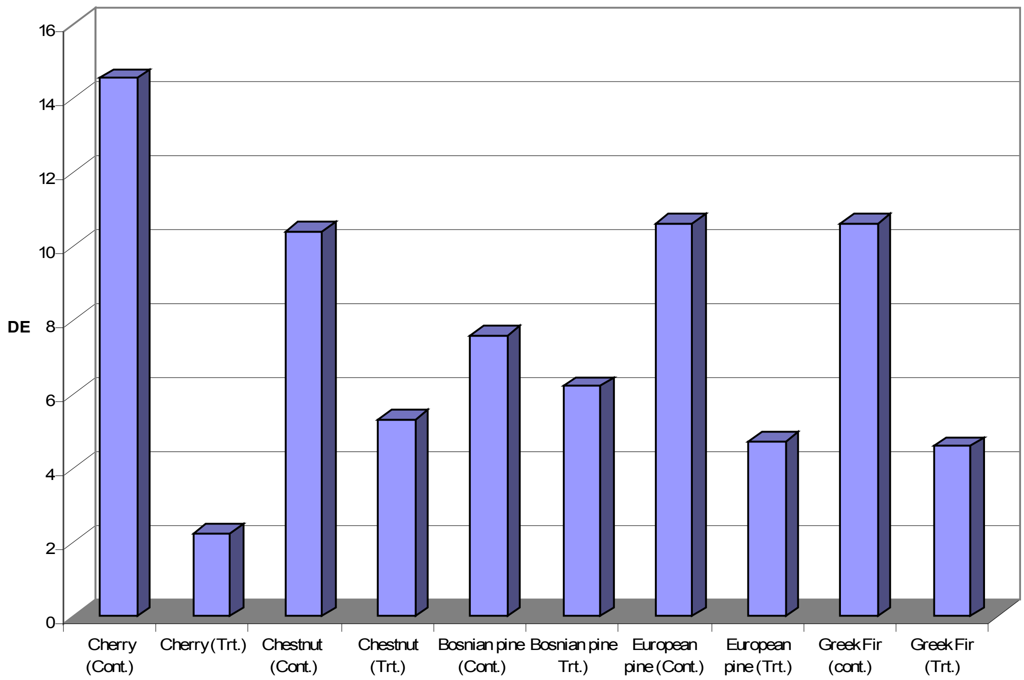

Fig. 1: Total colour difference (ΔE) of untreated and anti-UV treated woods

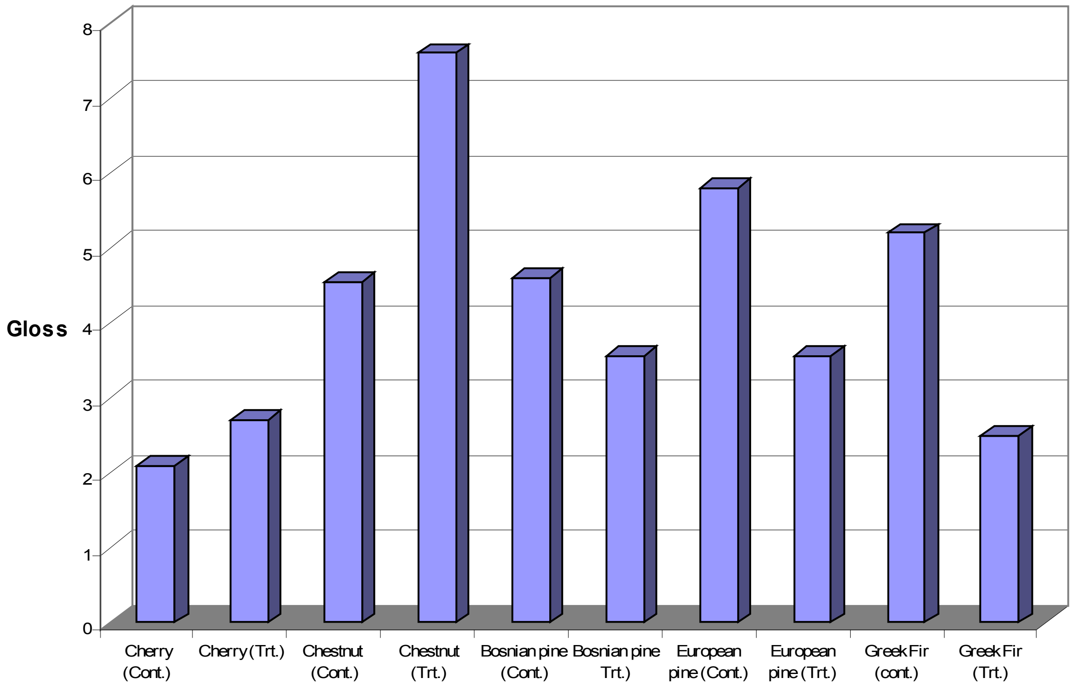

Fig. 2: The gloss (60 degree) properties of control and anti-UV treated wood

Tab. 1: Surface colour characteristics of untreated woods measured by CIE (1976) colour system (Values in metric).

Woods	**L* (lightness)**	**a* (green-red)**	**b* (blue-yellow)**	**C (Chroma)**	**H (Hue)**
Cherry	69.48	9.18	23.37	25.11	68.55
Chestnut	68.42	5.97	22.31	23.10	75.01
Bosnian Pine	71.1	9.3	29.87	31.28	72.70
European Pine	79.59	5.41	23.54	24.15	77.05
Greek Fir	75.88	5.54	26.26	26.84	78.08

Tab. 2: Surface colour characteristics of untreated and anti-UV treated wood measured by CIE (1976) colour system.

	ΔL	**% Improvement**	**Δa**	**% Improvement**	**Δb**	**% Improvement**
Cherry (Cont)	-9.57	79.4	4.86	91.6	9.8	107.9
Cherry (Trt.)	-1.97		0.41		-0.78	
Chestnut (Cont)	-4.85	4.32	2.04	57.8	8.23	129.6
Chestnut (Trt)	-4.64		0.86		-2.44	
Bosnian Pine (Cont)	-6.30	10.6	3.01	14.6	2.69	78.0
Bosnian Pine (Trt)	-5.63		2.57		0.59	
European Pine (Cont)	-5.95	48.1	2.68	45.5	8.37	61.3
European Pine (Trt)	-3.09		1.46		3.24	
Greek Fir (Cont)	-5.12	52.9	1.58	35.8	9.26	60.1
Greek Fir (Trt)	-2.41		1.05		3.69	

Tab. 3: Surface yellowness characteristics of wood measured by ASTM-D (1925)

Wood species	**Yellowness Index**
Cherry (Cont)	26.64
Cherry (Trt.)	0.58
Chestnut (Cont)	20.13
Chestnut (Trt)	0.45
Bosnian Pine (Cont)	12.01
Bosnian Pine (Trt)	7.61
European Pine (Cont)	18.49
European Pine (Trt)	8.16
Greek Fir (Cont)	19.01
Greek Fir (Trt)	8.28