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Accelerated Weathering Performance of Impregnated Wood Samples Coated with Zinc by Means of Plasma-Assisted Particle Deposition

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ACCELERATED WEATHERING PERFORMANCE OF IMPREGNATED WOOD SAMPLES COATED WITH ZINC BY MEANS OF PLASMA-ASSISTED PARTICLE DEPOSITION

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Abstract

Many different methods are currently applied for wood protection against outdoor conditions. The most important of these is the process of impregnation with liquid substances. However, this kind of wood preservatives cannot provide a long-term protection of wooden surfaces. Weathering-resistant surfaces can be obtained by applying UV absorbing agents. In this study, the influence of zinc particles applied by a plasma process at atmospheric pressure against UV light was investigated. First, wood samples were impregnated with boric acid, tall oil or copper azole. After impregnation, the samples were coated with zinc (Zn) particles, and coated and uncoated samples were exposed to accelerated weathering tests. The changes of the surface properties of the treated and untreated wood samples were studied by color changes, glossiness. Physical properties such as color changes, glossiness and surface roughness decreased for the samples coated with Zn particles. Brightness values also increased with the increasing weathering period.

Keywords: *Plasma coating, zinc (Zn) particles, impregnation, accelerated weathering*

Introduction

Wood and wood-based materials have been commonly used in the interior spaces for centuries and also constitute preferred multi-purpose materials for exterior applications. Unfortunately, wood is damaged by the exposure to various factors in the external environment (Zhang et al. 2009). These effects are UV light (ultraviolet rays), moisture (rain, snow, humidity, dew), mechanical forces (wind, sand, dirt), temperature, and atmospheric factors (O_2, SO_2, air, polluting gases). Those factors negatively affect the physical and chemical properties of wood-based materials (Hafizoglu and kilic 2007). UV light is one of the most important factors affecting wood and leads among others to color changes of wooden surfaces. These color changes occur more frequently in the wood's surface or near the surface. In addition to the loss of brightness, the surface roughness is increased and fissures in the wood are formed (Temiz et al. 2007). The resulting cracks lead to a higher surface area and permit a deeper penetration of, among others, the sunlight into the wood and therefore, they even accelerate the degradation of wood.

Degradation of wood by weathering primarily affects the wood components; in particular, it significantly reduces lignin and hemicellulose (Jin et al. 1991). Lignin is a good UV absorber and the chemical structure of lignin contains chromophoric groups, hence, lignin is sensitive to UV. Especially in the range from 295-400 nm (UV-A and UV-B), the absorption of light by wood was observed via the detection of discolouration and formation of chromophoric groups in wood (Feist and Hon 1984, Hon and Chang 1984, Zhang et al. 2009). UV radiation is absorbed by the wood and leads to the formation of free radicals which cause photodegradation of the wood. Photodegradation of wood starts with the oxidation of phenolic hydroxyl groups and causes a decrease of the methoxyl and lignin content consequently a change in color. In contrast, there is an increase in the rate of carboxyl groups and acidity (Fengel ve Wegener 1984, Zhang and Kandem 2000, Temiz 2005). These degradation components leach out of the wood by rain when being exposed to outdoor conditions (Fengel and Wegener 1984).

Various physical and chemical methods are applied for protecting wood from biological and physical degradation. Some surface modifications succeed in retarding degradation (Rehn et al. 2003). Impregnation, surface protective coating and varnishing are the most important surface protective treatments (Asandulesa et al. 2010). Copper compounds used during the impregnation process and the application of other metals or metal oxides that protect against UV may retard photo degradation.

Copper based compounds usually appear to be resistant to the UV rays as well as oil products. The surfaces cracks are reduced if oil compounds are used. Thus, they are considered to be resistant to weathering (Temiz 2005, Temiz et al. 2007).

A plasma treatment is a very promising method to improve the properties of wooden surfaces. In general, the plasma treatment technology using air as process gas is quite simple and the costs are rather low. In addition, this treatment process does not produce any environmental pollution (Pabelina et al. 2012). According to present knowledge, only the wood's surface is modified during such a process while no changes in mass or the structure of the wood (except on the surface) were observed. Hydroxyl, aldehyde, carboxyl and other polar functional groups are formed during a plasma treatment of the wooden surface (Acda et al. 2012). Plasma treatments are applied for two purposes. First, one can increase the polarity of the wood's surface; second, by adding substances to the plasma a deposition of protective coatings on the wood's surface can be achieved. For these purposes, a variety of gases and plasma methods can be applied (Denes et al. 1999, Podgorski et al. 2000, Rehn et al. 2003, Liu et al. 2010). However, the impact of these methods on the weathering performance of wood has not been studied yet.

The aim of the present study is to obtain an improved accelerated weathering performance of impregnated wood samples which were coated with zinc in a plasma process. Color changes and changes in glossiness were studied.

EXPERIMENTAL METHODS

Material

Scots Pine (*Pinus sylvestris L.*) specimens were prepared from sapwood blocks with dimensions of 15x75x150 mm (HxWxL) according to AWPA Standard E4-03. Three different chemicals were used for impregnation. The major constituents of the chemicals are given in Table 1 (Sivrikaya and Can 2013, URL 1, URL 2).

Table 1: Overview about the impregnation agents

Chemicals	Constituents	Proportion [%]
Copper azole	Copper carbonate	20,5
	2-aminoetanol	<20
	Boric acid	<5
	Tebuconazole	<0,5
	Propiconazole	<0,5
	Polyethyleneimine	<20
	Organic acid	<5
	Surfactant	<5
Boric acid	B_2O_3	56,25 min.
	SO_4	500 ppm max.
	Cl	10 ppm max.
	Fe	10 ppm max.
Tall oil	Fatty acids	52
	Resin acids	40
	Unsaponifiable matter	8

Impregnation procedure

The samples were impregnated with 2.4% copper azole (CA), 20% tall oil or 5% boric acid according to the ASTM D-1413 (1976) standard method. The reason for selecting these concentrations is that it is preferred for outdoor conditions. Literature studies tall oil and boric acid are used in these concentrations.While copper azole and boric acid were dissolved in water, tall oil was dissolved in ethanol. Pine wood (*Pinus sylvestris*) specimens were treated at 600 mm-Hg vacuum for 20 min and at a pressure of 6 bar for 60 min (ASTM-D 1413 1976). The retention content for each treatment was calculated by the following Equation (1).

$$R\left(\frac{Kg}{m3}\right) = \frac{G*C}{V} * 100 \quad (1)$$

Where G: (T2-T1) is the weight of the treatment solution (in grams) absorbed by the block (initial weight of the block subtracted from the initial weight plus the absorbed treatment solution); C is the weight of the chemical solution (in grams) in 100 g of the treatment solution; and V is the volume of the block in cubic centimeters.

Plasma treatment

The impregnated samples were coated with zinc powder by means of plasma-assisted particle deposition (Standart Zink flake GTT by Eckart Effect Pigments, d_{50}=13 µm). For this purpose, compressed air flows through the gap between two axially symmetrical electrodes. A pulsed high tension is applied to these electrodes causing an ionization of the air and hence, a formation of a plasma. Below the electrodes, a particle containing aerosol is added. These particles are melted and activated in the plasma and, due to the air flow, directed towards the substrate that is situated below this setup. At the same time, also the sample's surface is activated by the plasma leading to a relatively good bonding between the sample and the coating. By virtue of the facility's settings, it is possible to avoid a major heating of the substrate which permits a nondestructive coating of heat sensitive materials such as wood. Gas not used in the plasma treatment. Plasma processing conditions are applied; distance (1.6 mm), deposition speed (40-50 m/min), power (20-30 mm/h), pressure (1.2-1.6 bar), coating powder (pure zinc), powder sizes (13 µm). Surface contact angle after the plasma treatment could not be measured because surface very hydrophobic.

Accelerated weathering tests (QUV)
Weathering tests were performed by cycles of UV-light irradiation for 8 hours, water spray for 15 minutes and followed by a conditioning for 3.45 hours in an accelerated weathering test cycle chamber (ASTM G154 1998). The average irradiance level was 0.75 W/m^2 at 340 nm and the temperature in the chamber was approximately 50 °C. Two replicate samples of each treatment were exposed for 125 hours, 250 hours, 375 hours and 500 hours.

Surface characterization - Color measurements

Color measurements were performed according to ISO 7724. The CIELab system is described by three parameters: L* represents the lightness, a* and b* are the chromaticity coordinates; a*>0 describes red, a*<0 green, b*>0 yellow and b*<0 blue. L* varies from 100 (white) to zero (black).
The color coordinates L*, a* and b* were determined for each sample before and after the exposure to accelerated weathering. The color was measured by a color measurement device using a D65 light source. These values were used to calculate the color change ΔE* as a function of the UV irradiation period according to Equations (2) - (5).

$$\Delta L^* = L_f^* - L_i^* \quad (2)$$
$$\Delta a^* = a_f^* - a_i^* \quad (3)$$
$$\Delta b^* = b_f^* - b_i^* \quad (4)$$
$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}, \quad (5)$$

Where ΔL*, Δa*, and Δb* are the changes between the initial values and the values after certain time periods of exposure. A low ΔE* corresponds to a low color change or a stable color (ISO 7724-2 1984).

Glossiness
One of the first signs of ageing is the gradual loss of gloss of the surface. Gloss measurements were done using a KONICA Minolta Multi gloss 268 plus. The angle of incidence of the radiation was 60±0.1°, as defined in ISO 2813. Three measurements were made in each test sample, parallel to the application direction (ISO 2813 1994).

RESULTS AND DISCUSSION

Color measurements
The color coordinates of the samples before and after the deposition of Zn-particles are given in Table 2. The lightness (L*) values decreased in all samples after the coating process, while the redness (a*) and the yellowness (b*) values increased (table 2). After the coating process all samples' Lightness (L*) values decreased. The maximum change was observed for the copper azole treated samples. CuA treated samples have a green surface, but after the coating those samples tended towards a red color.

It can be stated that the chemical structure of tall oil is changed after plasma treatment. Moreover, the highest values in redness (a*) and yellowness (b*) were obtained for the samples treated with CuA. These CuA samples tend towards a red-blue color after coating.

Table 2: Color of wood samples before and after the deposition of Zn-particles, prior to the weathering procedure.

Variation	L*		a*		b*	
	uncoated	coated	uncoated	coated	uncoated	coated
Control	82.21	76.13	4.93	5.14	24.82	24.76
CuA	58.06	55.19	-5.01	-2.44	14.67	18.49
Tall oil	77.47	68.46	6.49	7.28	30.29	30.87
Boric acid	81.55	79.52	5.52	5.85	23.14	24.22

Figure 1 depicts the color changes (ΔL*, Δa*, Δb* and ΔE*) caused by different time periods of exposure to accelerated weathering. Positive or negative values of Δa* show a tendency of the wood's surface to become reddish or greenish, respectively, and yellowish or bluish for Δb*≠0. The Zn-coating turned the surface reddish and yellowish for the control and CuA. During the exposure to accelerated weathering, also the boric acid treated wood takes a reddish and yellowish color. The ΔL* values of all samples decreased during the first 125 hours of accelerated weathering, while the values of Δa*, Δb* and ΔE* increased. A slight decrease was observed for the impregnated and all Zn-coated samples, but the control samples' lightness value (ΔL*) decreased by 15% for an exposure of more than125 hour. For Zn-coated samples, the rate of white color is higher than for uncoated samples. In other words, the application of a Zn-coating leads to a trend towards a white color. After 500 hours of accelerated weathering, the least changes in lightness were observed for samples that were impregnated with tall oil (-0.12%) and coated with zinc.

The effectiveness of the tall oil may be attributed to its chemical content or might result from mechanical / physical protection in wood. Wood cell lumens are filled with tall oilThe maximum changes in Δa*, Δb* and ΔE* were observed for samples that were only impregnated with CuA. The color change slightly decreased by applying a Zn-coating (Temiz et al. 2003, Temiz et al. 2005, Temiz et al. 2007).

Extractives have a significant impact on the wood's natural color. Their structure can be degraded by a plasma treatment. Also as a result of a plasma treatment, free radicals appear on the surface of wood and these radicals may lead to discoloration of the wood's surface by reacting with oxygen (Sahin 2002). Zinc coated and weathered samples showed lower values of ΔE* than uncoated and weathered samples. This might result from the combination of different factors such as the plasma coating and weathering conditions (UV light or water). The color change is correlated to a lignin degradation and carbonyl formation which was studied by IR measurements. The IR peak at 1730 cm^{-1} (formation of carbonyl groups) and 1410 cm^{-1} (lignin degradation) and ΔE* are linearly correlated in the literature and also in our study (Muller et al. 2003). In our work, the control and tall oil treated samples' peak at 1452 cm^{-1} decreases and the peak at 1728 cm^{-1} increases after the plasma coating. Therefore, the plasma coating enhanced the color stability. Uncoated samples that were impregnated with CuA or boric acid showed an increase in both peaks. Color stability was not achieved because of the increase in both peaks.

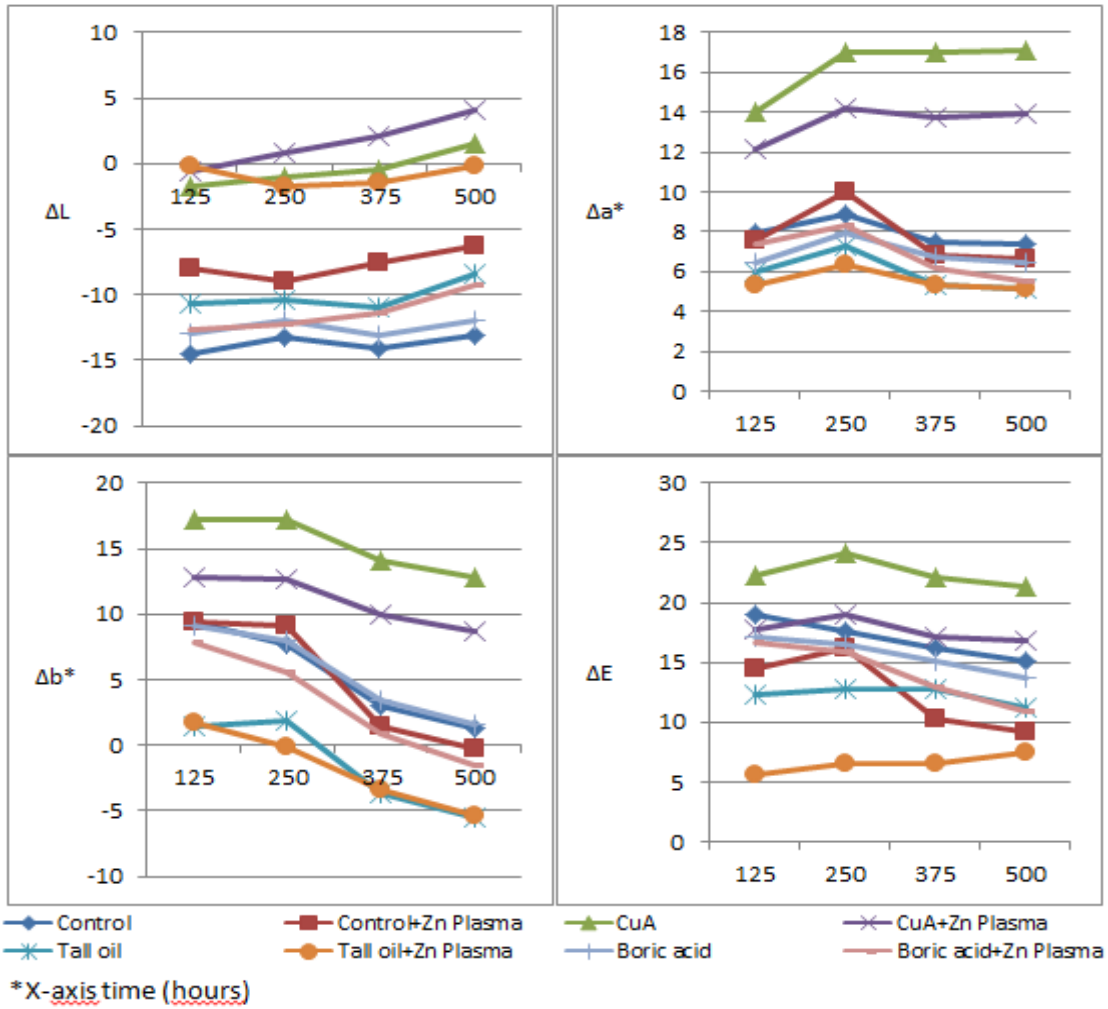

Figure 1: Colour changes of wood samples after exposure to accelerated weathering (%).

Glossiness

Glossiness values of wooden surfaces at an incidence angle of 60° were measured before and after the plasma coating, before and after accelerated weathering. The gloss change values (%) before and after accelerated weathering are given in Fig. 2 and 3, respectively.

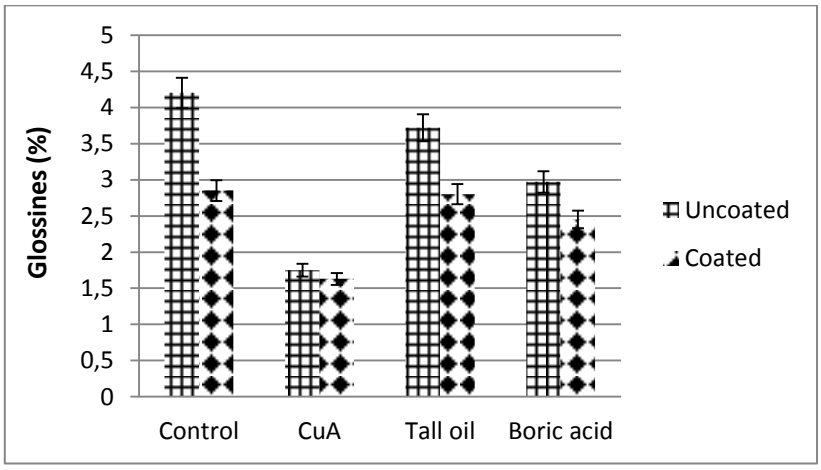

Figure 2: Glossiness of wood samples before and after the coating with zinc powder, prior to the weathering procedure.

The glossiness values of the samples decreased after the coating process due to the dark color of Zn. After the plasma coating, the maximum changes were observed for the control samples while the lowest changes were realized for samples impregnated with CuA.

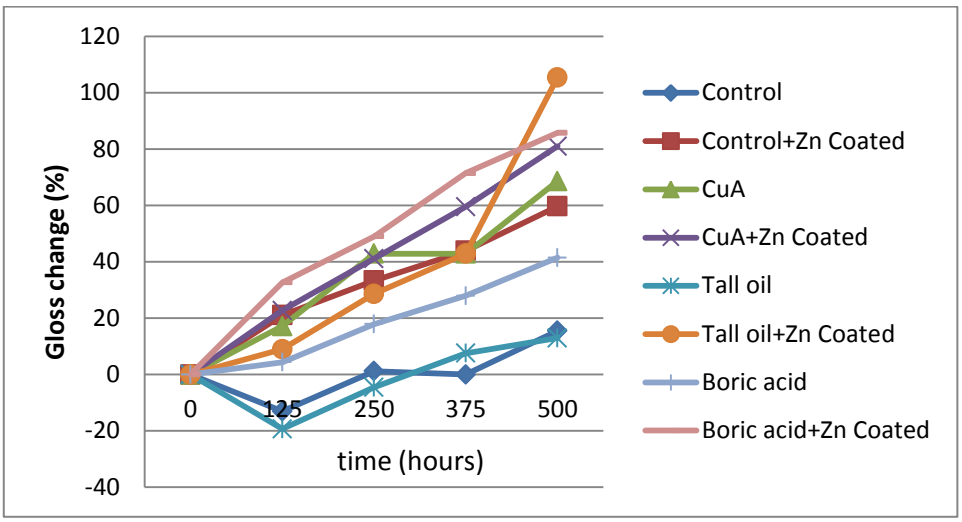

Figure 3: Gloss changes of wooden samples after accelerated weathering tests (%).

Prior to the weathering tests, the control and tall oil impregnated samples exhibited a darkened and dim surface, while glossy surfaces were obtained at a later time. All glossiness changes were higher for the Zn-coated samples than for their uncoated counterpart. Namely, glossier surfaces were obtained for Zn coated samples after the weathering tests. At the end of 500 hours the maximum change in glossiness is observed for the tall oil + Zn-coated sample, the least changes were obtained for the sample impregnated with tall oil (Fig. 3). The reason for higher changes in glossiness for the plasma coated samples is that Zn dust was washed out from the surface of the wood during accelerated weathering tests. As a result, glossier surfaces were obtained.

CONCLUSIONS

L*, a*, b*, and the glossiness values of the samples decreased and a darkening of the samples was observed after the plasma coating. After the weathering tests, the least changes of the color values were observed for tall oil, and the maximum color changes were obtained for a CuA treatment. Tall oil (with and without a subsequent plasma coating) provided a good color stability during weathering tests, however, it exhibited the maximum changes in glossiness. The cause of glossiness changes is thought to be Zn dust that is washed out from the surface of the wood during accelerated weathering tests.

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