Proceedings of the 11th Meeting of the **Northern European Network for Wood Sciences and Engineering** (WSE)

September 14-15, 2015

Poznan, Poland

Poznan University of Life Sciences

Faculty of Wood Technology

Edited by Waldemar Perdoch & Magdalena Broda

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Cover Design & Publisher

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PREFACE

There is an evident tendency in the recent global economy to fully utilize the natural renewable resources. One of the possibilities offered by our modern technology is to increase a raw material acquire. However, the increase of the efficiency of the raw material processing is even more important. I believe that the development and improvement of wood processing will be soon a key factor for economic progress in this part of Europe. Reviewing research topics of this Proceedings, I am all the more convinced that the mechanical and chemical wood processing, supported by our scientific projects, will play a significant role in the economy of the 21 century. Therefore, this Proceedings is dedicated to the researchers and students involved in wood science and technology as well as forest products engineering.

Prof. Dr Bartłomiej Mazela
Dean of the Faculty of Wood Technology
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IMPROVING THE PERFORMANCE OF SCOTCH PINE (*PINUS SYLVESTRIS*) WOOD SURFACE

Can, A.[1], Sivrikaya, H.[2]

ABSTRACT

In this study, the influence of wood stain (WS) and zinc (Zn) particles applied by a plasma process at atmospheric pressure against UV light was investigated. Scots Pine (*Pinus sylvestris L.*) specimens were prepared from sapwood blocks with dimensions of 15x75x150 mm (HxWxL) according to AWPA Standard E4-03. 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. The changes of the surface properties of the coated and uncoated wood samples were studied by color changes, glossiness and Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR) to analyze chemical changes on the samples' surfaces. Zinc coating and wood stain were provided color stability on wood surface. The glossiness of the samples surface was observed decreased after Zn coating, but increase parallel with weathering time, a decrease in WS application.

Key words: Zn coating, pine, discoloration, 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, local wood is damaged by the exposure to various factors in the external environment (Zhang et al. 2009)

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).

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Various physical and chemical methods are applied for protecting wood from biological and physical degradation. Impregnation, surface protective coating and varnishing are the most important surface protective treatments (Asandulesa and Topala 2010). Some surface modifications succeed in retarding degradation (Rehn et al. 2003). Coatings of wood surface with paint, varnish and modification with other chemicals improve the durability of wood surface against UV irradiation and weathering factors (Feist and Hon 1984, Temiz 2005, Temiz et al. 2005, Weichelt et al. 2011). However, over time chemical compounds leach out from wood surface and cause the environmental pollutions. The coatings to be applied on wood surface should be more resistant to weathering conditions (Hin et al. 1991, Temiz 2005)

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 Scots pine wood samples which were coated with zinc in a plasma process and wood stain. Color changes, glossiness and chemical changes were studied.

MATERIAL AND METHODS

Scots Pine (*Pinus sylvestris L.*) specimens were prepared from sapwood blocks with dimensions of 15x75x150 mm (HxWxL) according to AWPA Standard E4-03.

Hickson Decor Wood Stain (WS) was used as a coating material. 0.85 g/m2 of paint were applied to the wood surface. Samples were incubated in a day at room conditions and paint was applied in the same amount

Wood 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.

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. Wood samples were exposed for 125 hours, 250 hours, 375 hours and 500 hours.

Color measurements were performed wirth a Konica Minolta CM-600d. the reflection spectrum was acquired from a measuring area of 8 mm in the 400 to 700 nm wavelength range, where three measurements at precisely defined points on the weathered surface of each sample were carried out periodically (ISO 7724-1). The CIE (Commissions Internationale de I'Eclairage) color parameters L* (lightness), a* (along the X axis red (+) to green (-)), and b* (along the Y axis yellow (+) to blue (-)) were calculated. Color diffirences ΔE* were calculated according to Eq. 1.

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

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).

FTIR analysis has been used as a technique to obtain information about the structure of the wood constituents and chemical changes taking place in the wood during the plasma and the weathering process. FTIR spectra were obtained by a Shimadzu IRAAffinity-1 equipped with a Single Reflection ATR pike MIRacle sampling accessory. Four accumulated spectra with a resolution of 4 cm^{-1} were obtained for wavenumbers from 800 cm^{-1}- 1800 cm^{-1} with 32 scans for each sample.

RESULTS and DISCUSSION

Color measurements

The color coordinates of the samples before and after the deposition of Zn-particles and wood stain are given in Table 1. The lightness (L*) values decreased in all samples after the coating process, while the redness (a*) and the yellowness (b*) values increased (table 1). The maximum change was observed for the together with the implementation of plasma and wood stain treated samples. When wood are exposed the plasma and wood stain, its color tended towards a red color.

Table 1 Color of wood samples before and after the deposition of Zn-particles and wood stain, prior to the weathering procedure.

Variation	L*	a*	b*
Control	82,21 ± 1,15	4,93 ± 0,58	24,82 ± 2,53)
Control+ Zn coating	76,13 ± 2,38	5,14 ± 0,58	24,76 ± 2,53)
Control+WS	62,17 ± 4,94	22,71 ± 4,00	52,94 ± 2,43)
Control+ Zn coating +WS	59,54 ± 2,16	24,57 ± 0,79	53,58 ± 2,91)

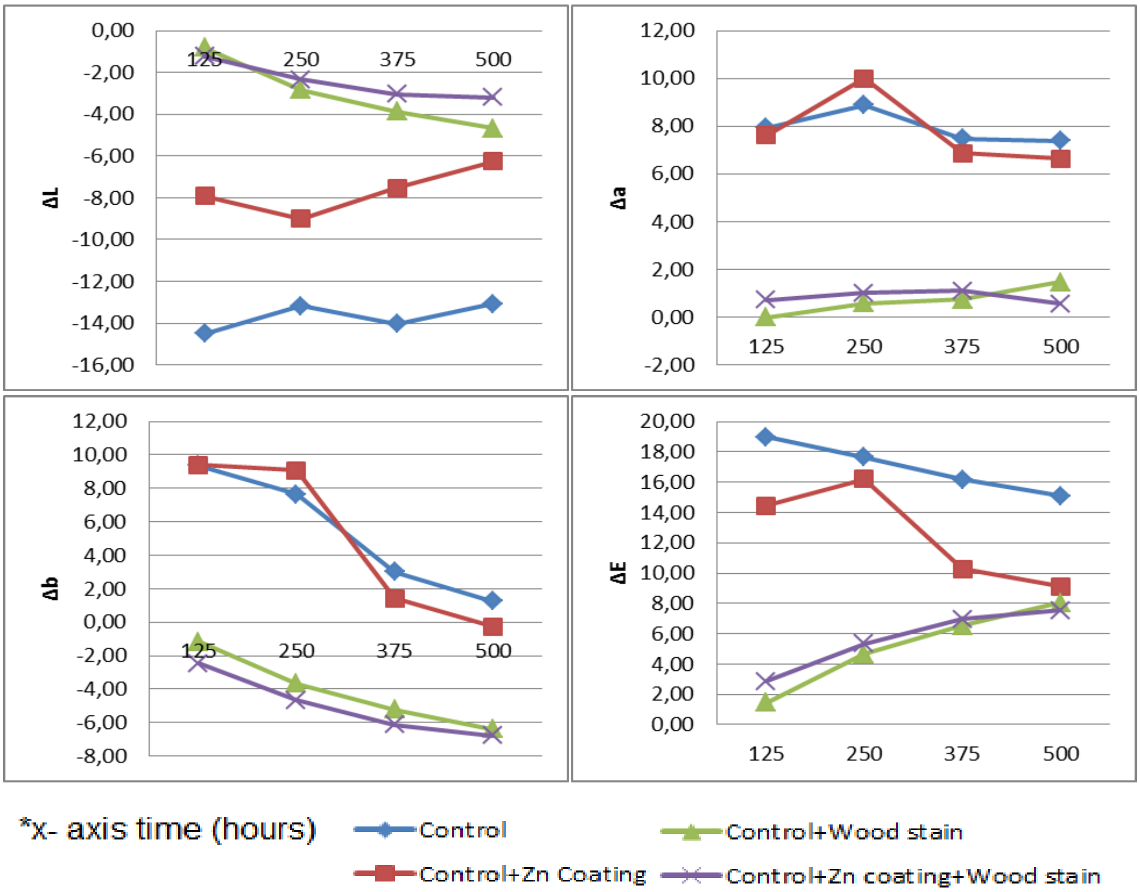

Fig.1 Colour changes of wood samples after exposure to accelerated weathering (%).

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 (Hunter 2008). The Zn-coating turned the surface reddish and yellowish for the control. The ΔL* values of all samples decreased during the first 125 hours of accelerated weathering, while the values of Δa* and ΔE* increased. A slight decrease was observed for the WS coated samples, but the control samples' lightness value (ΔL*) decreased by 15% for an exposure of more than125 hour. After 500 hours of accelerated weathering, for WS samples, the rate of white color is higher than other samples. In other words, the application of a WS leads to a trend towards a white color.

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 control sample. This might result from the combination of different factors such as the plasma coating and weathering conditions (UV light or water). In addition to contact with the wood surface of UV rays are blocked by the WS application. The best result was obtained as a result of control+Zn coating+WS application.

Glossiness

Glossiness values of wooden surfaces at an incidence angle of 60° were measured before and after the plasma coating and WS, before and after accelerated weathering. The gloss values are given in Table 2.

Table 2 Glossiness of wood samples before and after the coating with zinc powder and wood stain

Variation	Before weathering	After weathering			
		125 Hours	250 Hours	375 Hours	500 Hours
Control	4,2 ± 0,25	3,6 ± 0,78	4,2 ± 0,40	4,2 ± 0,30	4,8 ± 0,45
Control+WS	26,7 ± 1,26	8,0 ± 2,83	7,2 ± 3,18	6,4 ± 0,20	6,3 ± 0,30
Control+ Zn coating	2,8 ± 0,28	3,4 ± 0,35	3,8 ± 0,49	4,1 ± 0,30	4,5 ± 0,30
Control+ Zn coating +WS	37,6 ± 4,23	13,6 ± 1,06	10,3 ± 0,42	9,3 ± 0,60	8,7 ± 0,35

The glossiness values of the samples decreased after the coating process due to the dark color of Zn, but after the paint application highly gloss surface was obtained. After the weathering test glossier surfaces were obtained for Zn coated samples. 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. At the end of 500 hours the maximum change in glossiness is observed for the WS application sample, the least changes were obtained for the control sample (Table 2).

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR)

While investigating the effect of weathering on plasma, WS coated and uncoated wood, the attention has been focused on the changes of the absorption intensity at 1720-1740, 1508, 1457, 1261, 1155 and 1025 cm^{-1}. The intensity and changes of these bands are related to changes of the chemical structure of wood components (Temiz et al. 2003, Temiz et al. 2007, Liu et al. 2010, Aydın and Demirkir 2010, Huang et al. 2013, Yildiz et al. 2013, Fufa et al. 2013).

After the Zn coating, polar groups such as C-O and C=O increase and non-polar groups such as C-C and C-H decrease on the wood's surface (Aydın and Demirkir 2010)

Table 3 Variation of the average absorbance values of the different samples before and after weathering.

Variation	1024	1155	1235	1452	1510	1728
Control	0.106	0.048	0.039	0.033	0.026	0.018
Control+Zn coating	0.105	0.046	0.390	0.033	0.029	0.019
Control+WS	0,134	0,053	0,042	0,034	0,028	0,020
Control+weathering	0.132	0.116	0.097	0.070	0.035	0.151
Control+ Zn coating+weathering	0.066	0.052	0.043	0.030	0.017	0.063
Control+WS+weathering	0,082	0,041	0,035	0,029	0,024	0,023
Control+Zn coating+WS	0,100	0,043	0,037	0,032	0,025	0,018
Control+Zn coating+WS+weathering	0,112	0,045	0,036	0,030	0,029	0,015

Because of UV light degradation 1720-1745 cm^{-1} carbonyl absorption peaks are increase which reported some researchers. An increase was found for the carbonyl absorption band at 1728 cm^{-1} in all variation of our study. Pandey reported the same results for their study about weathering of untreated chir pine and rubber wood (Pandey 2005, Ozgenc et al. 2013).

The absorbance peak around 1510 cm^{-1} describes the lignin because of the C=C stretching of the aromatic ring present in lignin. The peak usually appears between 1515-1500 cm^{-1} (Pandey 2005). The peak at 1515 cm^{-1} decreased after exposure to weathering of the Zn coated samples while increased after the WS application.

The peak at 1235 cm^{-1} corresponds to the syringyl group and the peak at 1452 cm^{-1} is associated with the C-H asymmetric bending of CH_3 in lignin (Colom et al. 2003). The decrease in intensity of these two peaks occurred after the plasma coating, but 1452 cm^{-1} peak are decreased because of Zn coated samples which exposed to weathering. WS applied samples showed a decrease in both peak after weathering.

The changes of the peaks at 1155 cm^{-1} and 1024 cm^{-1} for the plasma coated samples are assumed to be related to a modification of cellulose and hemicellulose. These peaks decreased for the Zn coating while these peaks increased after WS, and weathering of control. But, WS and Zn coated samples when exposed the weathering, these two peaks are decreased.

CONCLUSIONS

L*, a*, b*, and the glossiness values of the samples decreased and a darkening of the samples was observed after the plasma coating, but a*, b*, and the glossiness values of the samples increased was observed after the WS coating. After the weathering tests, the least changes of the color values were observed for Zn coating and WS combination, and the maximum color changes were obtained for a control samples. Zn coating and WS combination 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 WS that is have light color during accelerated weathering tests. Also the Zn coating and WS yielded a good color stability of samples, which is also supported by ATR-FTIR results. The peak at 1728 cm^{-1} increased for plasma coated and WS samples after weathering.

ACKNOWLEDGEMENTS

I would like to thank you very much for the friendly cooperation to Lena Wallenhorst, Wolfgang Viöl and Holger Militz.

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