# EFFECTS OF NANO-ZINC OXIDE BASED PAINT ON WEATHERING PERFORMANCE OF COATED WOOD

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# ABSTRACT

This work describes the effect of the nanoparticles and paint performance on accelerated weathering performance of coated specimens. Nano-sized zinc oxide (ZnO) was chosen as a suitable candidate for the UV-protection of coatings. The accelerated weathering performances of Scots pine coated with wood paint mixed with nano- ZnO were investigated. Uncoated specimens, specimens coated with only nano-ZnO and nano-zinc oxide based paint were used as references. 1 ml and 3 ml nano-zinc oxide is added into the 1 ml and 3 ml paint particularly. The samples were exposed to an accelerated weathering test for duration of 22 days in a QUV cabin for 18 minutes and a two-hour ultraviolet (UV) cycle. Colour and gloss change were used to investigate to change after several intervals (0-4-10-14-22 days) in accelerated weathering of coated and uncoated wood. In general, while the addition of nano-ZnO in paint resulted in negative effects on color change, total color change of wood samples which exposed to nano-ZnO subsequent to paint less than uncoated wood. Addition of nano-ZnO slightly decreased glossiness compared to paint and uncoated samples.

#### **1** INTRODUCTION

The use of wood and wood products in outdoor and buildings has long been of interest due to its important feature. However, it is well known that wood is sensitive material to natural weathering conditions which mainly cause a loss of original color and surface fibers. Degradation in wood by weathering significantly reduces esthetic appearance. The main cause of discoloration is degradation of lignin by UV- irradiation and water (Feist et al.1984; Yildiz et al. 2013). Lignin is a good UV absorber and is quickly structural degraded because of the chromophoric groups (Ozgenc 2012).

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 et al. 1984; Temiz et al. 2005; Temiz 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. Different chemicals and surface processes are implemented to resolve these drawbacks. The durability of exterior wood clear coatings contains nanosized inorganic UV absorbers. ZnO and TiO<sub>2</sub> are used for improving wood surfaces against to UV radiation, water, mildew, fungus growth, stains and grease (Vlad Cristea et al. 2012). Zinc oxide has been used for a long time as an UV stabilizer and preservative component in wood coatings (Carol et al. 2010).

Performance of coatings incorporated with zinc oxide (ZnO) into polypropylene, maleic anhydride modified polypropylene and polyurethane coatings restricted the color changes and photo degradation of wood polymers (Salla et al. 2012; Zhao and Robert 2006).

Fufa et al. (2012) found that the coated specimens exhibited lower color changes than uncoated specimens in the early stages of weathering. Namely coating to retard the early color changes of the specimens. They also indicated that the coating was removed from wood surface in the long exposure period due to the UV and water. Therefore, color changes of the coated specimens become the highest at long period. If coatings are contains nanoparticles, modified wood exhibit better performance than unmodified wood surface (Fufa et al. 2012)

The objective of this work is to evaluate the effectiveness of nanoparticles in delaying the photodegradation of wood stain coatings applied to Scots pine. This work describes the effect of the nanoparticles and wood stain performance of wood stain by accelerated weathering. 1 ml and 3 ml nano-zinc oxide is added into the 1 ml and 3 ml paint particularly.

## 2 MATERIALS AND METHODS

#### 2.1 Materials

Specimens of Scots pine (*Pinus sylvestris*) of size 15 x 75 x 150 mm (radial x tangential x longitudinal) were prepared from defect free wood.

#### 2.2 Coating of wood surface with nano ZnO and dispersed wood stain

Nano-zinc oxide (NANOBYK-3841) was provided as an aqueous dispersion containing 40% 40 nm zinc oxide particles with a dispersant (Methoxypropylacetate).

Hickson Decor Wood Stain was used as a coating material, and nano ZnO as an additive 8 different variations were performed in this experiment as shown in Table 1. There are eight different groups in the study. First, 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. 3 and 1 ml nano-ZnO was applied with brush surface of C and D groups' a coat of paint. 1/1 ratio nano-ZnO and paint mixed and was applied to the wood surface groups E and F. As to groups G and H, paint was applied with brush after nano-ZnO is dried applied to the wood surface.

Pre-weathering test specimens that were conditioned to 21 °C and 65% relative humidity (RH) for a week.

Group	Variation
A	Control
В	Paint
С	3 ml ZnO
D	1 ml ZnO
E	Paint+3ml ZnO
F	Paint+1ml ZnO
G	3ml ZnO+Paint
Н	1ml ZnO+Paint

#### Table 1. Sample groups

#### 2.3 Accelerated weathering test

The weathering experiment was performed by cycles of UV-light irradiation for 2 hours followed by a water spray for 18 minutes in an Accelerated Weathering Test Cycle chamber (ASTM G-53). The average irradiance was about at 340 nm and the temperature in the chamber was approximately 50 °C. Two replicate samples of each treatment were run for 4 days, 10 days, 14 days and 22 days.

#### 2.4 Color measurements

Color measurement was determined according to ISO 7724 Standard. The CIELab system is described by three parameters: L\* axis represents the lightness, a\* and b\* are the chromaticity coordinates; +a\* for red, -a\* for green, +b\* for yellow and -b\* for blue. The L\* varies from 100 (white) to zero (black).

L<sup>\*</sup>, a<sup>\*</sup> and b<sup>\*</sup> color coordinates for each sample was determined before and after exposure to accelerated weathering. The color was measured on a color measurement devise using a D65 light source. These value were used to calculate the color change  $\Delta E^*$  as a function of the UV irradiation period according to Equations (1), (2), (3), and (4).

$$\Delta L^* = L_f^* - L_i^*$$
 ...(1)  
 $\Delta a^* = a_f^* - a_i^*$  ...(2)

$$\Delta b^* = b_f^* - b_i^* \qquad \dots (3)$$

$$\Delta \mathsf{E}^* = \sqrt{\Delta L *^2 + \Delta a *^2 + \Delta b *^2} \qquad \dots (4)$$

Where,  $\Delta L^*$ ,  $\Delta a^*$ , and  $\Delta b^*$  are the changes between the initial and several intervals values. L\*, a\*, and b\* contribute to the color change  $\Delta E^*$ . A low  $\Delta E^*$  corresponds to a low color change or a stable color.

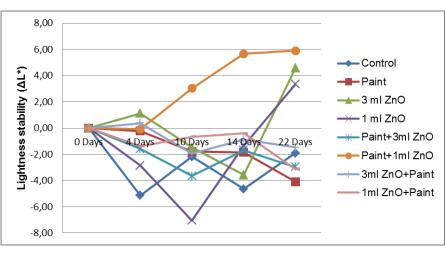
#### 2.5 Glossiness

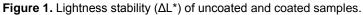
One of the first signs of ageing is the gradual loss of gloss of the coating film. Gloss measurements were taken in a KONICA Minolta Multi gloss 268 plus. The angle of incidence of the radiation was  $60\pm0.1^{\circ}$ , as defined in ISO 2813. Six measurements were made in each test panel, three parallel to the application direction and three perpendicularly.

## 3 RESULTS AND DISCUSSION

#### **Color measurement**

Irradiation time of the color changes ( $\Delta E^*$ ), Lightness stability ( $\Delta L^*$ ), Red-green stability ( $\Delta a^*$ ), and Yellow-blue stability ( $\Delta b^*$ ) of coated and uncoated samples is represented in Figure 1-4 respectively.



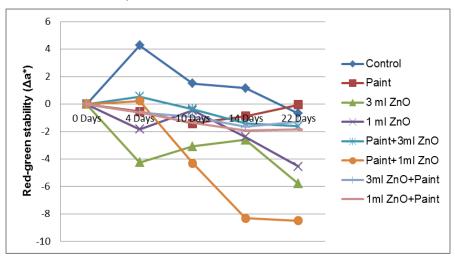


It is well known that decreasing in L value implies occurring darkness on wood surface, whereas increasing states the lightness (Yildiz et al. 2013). The wood surface tends to be darkening in case of the surface treatment. Figure 1 indicates that the maximum change in lightness was obtained in control samples; however the lightness decreased initially in the experiment. While the samples of control and F group showed increasing, the other coated samples continued to decrease after 4 days exposition. The total 22-day period exhibited the lower lightness in comparison to initial value except for C, D, and F groups, and the samples in the group of G had the highest change. 3 ml nano-ZnO + paint showed the lowest change to 22 days. According to Feist et al.(1984) the negative value in light stability demonstrates the sensitivity, caused by UV, on the wood surface.

#### Session Wood modification processes

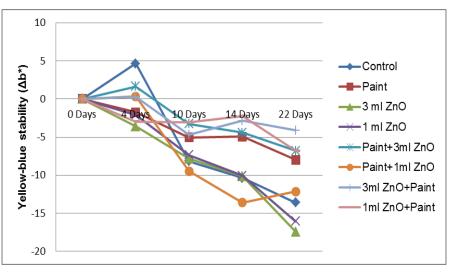
Likewise, the lightness was appeared in the "F" samples, whereas the samples of "B " revealed the most darkness after 22 days accelerated weathering.

The lowest differences on the red–green scale were exhibited in coated with paint ( $\Delta$ a:-0,05) and control ( $\Delta$ a:-0,69) samples whereas paint+1ml nano-ZnO ( $\Delta$ a:-8,48) and 3ml nano-ZnO ( $\Delta$ a:-5,79) showed the highest variation of the same scale (Fig. 2) after 22 days. Application of paint after 1 ml and 3 ml nano-ZnO yielded the same red – green value The similar results were obtained when the post treatment coating applied to ZnO coated (1 and 3 ml) samples that resulted in insignificant change in  $\Delta$ a\*. The application of paint generally resulted in a trend towards the green color which was a concluded mark in this study.



**Figure 2.** Red-green stability ( $\Delta a^*$ ) of uncoated and coated samples.

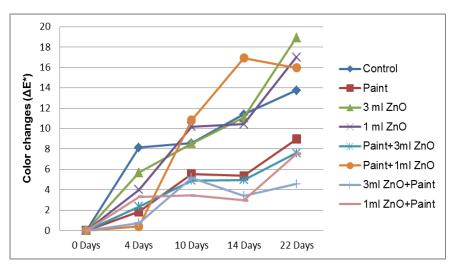
The color turned to be blue after 4 days aging (Fig. 2). The maximum change in blue-green color occurred with 3-1 ml nano-ZnO that was attributed to the leaching of nano-ZnO during the experiment. Because, no treatment was applied after nano-ZnO application.



**Figure 3.** Yellow-blue stability ( $\Delta b^*$ ) of uncoated and coated samples.

The total color change of all samples was increased in the early stage of exposure (Fig. 4). This increase reached a maximum at the end of 22 days. The highest color change was determined for coated with 3 ml nano-ZnO ( $\Delta$ E:18,93) and 1 ml nano-ZnO ( $\Delta$ E:17), while the lowest color change was found for coated with 3 ml nano-ZnO + paint ( $\Delta$ E:4,58). 1 ml ve 3 ml nano-ZnO application gave the best result when compared to other treatments. The possible reason might be the nano-ZnO remained on the surface. Because, paint application prevented the leaching of nano-ZnO from the wood surface. Current study showed that nano ZnO compounds could be used with coatings because of the UV

resistance. It was also correlated with literature findings. (Clausen et al.2010; Mahltig et al.2010; Weichelt et al. 2011).



**Figure 4.** Color changes ( $\Delta E^*$ ) of uncoated and coated samples.

#### Glossiness

Glossiness values of wood surfaces at a 60° incidence angle, measured before and after accelerated weathering, and gloss change values (%) after accelerated weathering were given in Fig. 5. Glossiness is described that a reflection of the light like a mirror, thus It is very important to aesthetic and decorative view of the coated surfaces. (Cakıcıer et al. 2011). Unlike the ZnO samples (3 and 1 ml), the glossiness decreased in other treatments during the weathering. It might be caused from cracks, physical and biological degradation on the wood surfaces (Christy et al. 2005; Bucur 2011; Karamanoglu 2012). The glossiness values of the coated and control samples were measured initially 9,7 and 26,6, and after the test as follow 7,55, 5,6. The significant loss in glossiness was shown in control samples.

Accelerated weathering slightly effect on the glossiness of specimens. Scrinzi *et al.* restricted the UV effect when they applied the coating on wood surface. In addition, coatings may improve the glossiness of the wood surface. It can be seen that coating enhances gloss of wood surface. The highest glossiness change was obtained in control, whereas the minimum in the group of F. (Fig. 5).

The glossiness change in F was 50 times lower than controls. No significant difference was found in the other treatments.

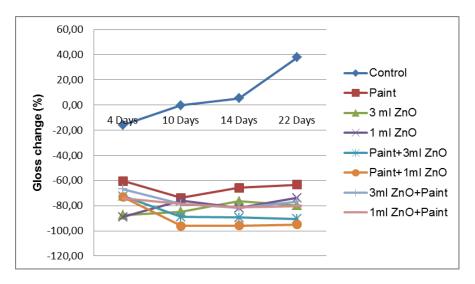


Figure 5. Gloss changes of uncoated and coated samples.

#### Conclusions

Unpainted specimens exhibited higher color changes than coated specimens with paint in the early and long stages of exposure. This may indicate the capacity of coating to retard the early color changes. Performance of nano-ZnO was relatively low due to removal of the nano-ZnO from the specimens surface by water. Nanoparticles of ZnO have the ability to offer UV protection to coatings so it was low discoloration than from the use of only nano-ZnO. Further studies are needed on the painted wood with pretreated nano-ZnO to prevent leaching of nano-ZnO.

Accelerating weathering test concluded that wood surface became dark expect for control samples. In addition, the brightness value varied on the wood surface during the weathering process.

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