

COLOR STABILITY FOR WOOD PRODUCTS DURING USE: EFFECTS OF INORGANIC NANOPARTICLES

Vincent Blanchard* and Pierre Blanchet

Despite significant progress having been achieved in recent years to improve wood's durability, additional developments are still necessary to increase its color stability. ZnO and CeO₂ nanoparticles were compared to UV absorbers (Tinuvin 477 DW, 292 and 5151) commonly used to stabilize the wood products color. Nanoparticles, with concentrations in the range 1 to 2 wt%, and UV absorbers, using concentrations advised by the manufacturer, were dispersed in a waterborne UV curable polyurethane/polyacrylate resin. Dispersions were carried out with a high speed mixer at 2,500 RPM with micro glass beads or not, depending on the form of the nanoparticles. Nanocomposite coatings were aged with a weather-o-meter (CI 3000+ - Atlas) according ASTM G155. Color variations were measured with a colorimeter (BYK Gardner – Color Guide 45/0) working with the CIE L*a*b* system. The aim of the present study was to assess the effects of inorganic UV absorbers on the stabilization of color under indoor conditions. Results showed that nanoparticles (ZnO, CeO₂) absorbed UV light frequencies in a manner similar to common organic molecules. Their efficiency was better at medium durations of light exposure, for which they could achieve the action of organic absorbers. Finally, the simultaneous use of both absorbers seems to create a protective synergy when degradation is due to UV energy alone.

Keywords: Nanoparticles; Wood color; Color stability; Photo-oxidation; Photo-degradation; ZnO; CeO₂; Ultra-violet light

*Contact information: FPInnovations, 319 rue Franquet, Quebec City, Canada, G1P 1R4. *Corresponding author: vincent.blanchard@fpinnovations.ca*

INTRODUCTION

Relative to the appearance of wood products, wood discoloration is a major problem. It is common to observe important differences in how different wood products become discolored when exposed to environments that contain UV light. A typical situation may involve an area rug on hardwood flooring in front of a window door, where the color of the wood under the rug remains unchanged, revealing the extent of changes in the adjacent flooring beside the rug. For indoor products, the main attack is the result of the photo-degradation of wood due to solar radiation (Aloui et al. 2007; Mazet et al. 1993; Hon 1990). Of the three main components of wood, lignin is the most prone to photo-oxidation because of its chromophores (Kiguchi et al. 2001; Evans et al. 1996). Three types of UV rays are emitted by the sun, UV A, UV B, and UV C. Of these, only the UV A can go through window glass, and such radiation falls within a wavelength range of 315 to 400 nm (Grossman 1990). George et al. (2005) mentioned that visible light also can cause discoloration, especially for colored materials such as wood.

The oxidation of natural or synthetic polymers is also a significant factor. Triboulot (1993) showed that Vancouver fir yellowing is directly linked to the rate of oxidation. Podgorski (1993) explained that oxidation is based on free radical reactions that only occur on the wood surface. Protective coatings can in principle limit this process, but they are known to become inefficient when cracks appear (Hayoz et al. 2003; Buckle et al. 2005).

The action of water is as complex as that of UV radiation. Many studies have demonstrated that water can initiate chemical and physic-chemical reactions (Searle 1984; Grossman 1990; Podgorski 1993). Water can interact with coating/wood systems in different ways, including full immersion, streaming, condensation, and interaction with ambient humidity. The latter is the most important in terms of interior uses. Chemically, water leads to hydrolysis reactions with both wood and with coatings (Bauer 2000).

Podgorski (1993) and Aloui (2006) explained that ambient temperature directly influences intrinsic polymer properties. Indeed, when temperature is below the glass transition point, the macromolecular network is fixed, a situation that strongly limits degradation reactions.

There are several strategies to maintain the original colors of an object, and these are briefly listed below:

- Quenchers deactivate excited states of the molecules by transfers of electrons or energy, or by chemical mechanisms.
- UV absorbers absorb UV energy and release it as heat energy or fluorescence.
- H-donors release hydrogenous atoms to neutralize free-radicals.
- Radical scavengers react with all free radicals released in degradation reactions.
- Hydroperoxide decomposers release alcohols to neutralize hydroxyl and alkyl radicals that contribute to degradation mechanisms.

Most of the mechanisms listed above are based on organic molecules. However, inorganic UV-absorbers are now available at a nanometer scale. Metal oxides could be added in the formulation of transparent and semi-transparent coatings such as varnishes used for flooring.

Previous studies have considered the use of inorganic UV absorbers for the protection of biomaterials, such as the cellulose in textiles (Wang et al. 2004, 2005). Many types of nanoparticles have been synthesized for this purpose. This technology could easily be used in the preparation of transparent and semi-transparent coatings. The properties of nanoparticles are mainly driven by surface atoms because of the large specific surface area, which explains the difference in term of chemical-physical properties in comparison with microscopic particles, the properties of which are dominated by bulk atoms.

The aim of the present work was to assess the efficiency of inorganic nanoparticles in absorbing UV radiation in order to stabilize the color of wood . Two types of nanoparticles were selected: zinc and cerium oxides in powder or pre-dispersed in water forms. They were added to the formulation of a waterborne UV-curable polyurethane/polyacrylate coating. Nanoparticle dispersions were characterized by transmission electron microscopy (TEM), and accelerated aging was carried out with a weather-ometer. The color variation was studied with the CIE L*a*b* system.

MATERIAL AND METHODS

The wood species used in this study was sugar maple (*Acer saccharum*), as the whiteness of this wood is an important aesthetic characteristic of the species. All the specimens were obtained from the same board. All the specimens were conditioned at 20 °C and 50% relative humidity until constant mass and sanded at 150-grit before treatment. Each series consisted of 5 tangential longitudinal specimens, each 4 x 85 x 100 mm in thickness, length, and width, respectively.

A waterborne UV-curable polyurethane/polyacrylate resin was applied to the wood surface. The components and their formulations were supplied by an industrial partner. The coating was applied with a roller coater (Holytech – ATG 012005) for a thickness of 3×10^{-5} m, and then dried in two steps. It was first flashed at 60°C for 10 minutes for water evaporation and polyacrylate cross-linkage. In the second step, it was exposed to UV radiation to cross-link the polyurethane (Sunkist mercury lamp / UVA = 530 mJ.cm⁻²) and to complete the curing process.

The nanoparticles selected were zinc and cerium oxides in powder and water pre-dispersed forms; properties are summarized in Table 1. They were directly added to the waterborne resin at the beginning of formulation and dispersed with a high speed mixer (Ragogna Custom Machinery – Model designed for painting manufactures). Blending was performed at 2,500 RPM to avoid destabilizing polymer emulsions. For powders, micro glass beads were used to increase the shear rate to improve the nanoparticle dispersion. Moreover, coatings were promptly applied on the wood surface (within a few hours) in order to limit particle aggregation. These nanocomposite coatings were compared among themselves and with reference coatings (with organic UV absorbers Tinuvin 477DW and 292 from the Ciba Company).

Table 1. UV Organic and Inorganic UV Absorbers

Type	Trademark	Composition	State	Company	Particles size (nm)
Inorganic	NanoByk 3820	ZnO	liquid	BYK-Chemie	20
	NanoByk 3840	ZnO	liquid	BYK-Chemie	40
	Nanoshield Zn 2000	ZnO	liquid	Alfa Aesar	1-100
	Rhodigard S100	CeO ₂	liquid	Rhodia	10
	NanoTek CE6042	CeO ₂	liquid	Alfa Aesar	1-100
	VP Adnano ZnO 20	ZnO	Powder	Evonik-Degussa	0-100
Organic	Tinuvin 477 DW	Hydroxy-phenyl-triazine derivative	liquid	Ciba	Not Applicable
	Tinuvin 292	<i>Bis</i> (1,2,2,6,6-pentamethyl-4-piperidyl) sebacate et Methyl 1,2,2,6,6-pentamethyl-4-piperidyl sebacate	liquid	Ciba	Not Applicable
	Tinuvin 5151	<i>Tinuvin 477 DW and 292 mixture</i>	liquid	Ciba	N/A

Nanoparticle dispersions were characterized by transmission electronic microscopy (TEM), using a Jeol 1230 instrument. Films were deposited on a copper grid support. An acceleration voltage of 80 kV was used to record pictures. The UV/visible absorption spectra of nanoparticles were characterized and compared to organic UV absorbers used as reference. Different dispersions are summarized in Table 2.

Table 2. Concentrations in wt% of UV Organic and Inorganic Absorber Combinations

Mixture	Tinuvin 477 DW	Tinuvin 292	Nano-Byk 3820	Nano-Byk 3840	Nano-shield Zn2000	Rhodi-gard S100	Nano-Tek CE6042	VP Adnano ZnO 20
1	5	1						
2			1					
3				1				
4					1			
5						1		
6							1	
7								1
8				1.5				
9					2			
10				0.5		0.5		
11	5	1		1				
12								2

Accelerated aging was done with a xenon-arc Weather-OMeter CI 3000+ (Atlas) according ASTM G155. For accelerated wood/coating aging, specimens were exposed to continuous UV radiation for 400 hours with a filter combination Boro-S / Boro-S to simulate an outside exposure to increase UV degradation, and so reduce testing time. The relative humidity was about 35%, the UV/Visible radiation range was between 340 and 800 nm, the spectral irradiance was 0.35 W/m^2 , and the temperature was $63 \pm 2.5^\circ\text{C}$.

The specimens color variation due to accelerated aging was assessed with a colorimeter (BYK-Gardner – Color Guide 45/0) working with the CIE $L^*a^*b^*$ system. The parameters L^* , a^* , and b^* represent the lightness, green/red, and blue/yellow components respectively. Measurements were done according to ASTM 224. Color components were measured every 24 hours at the beginning, but the time period between successive measurements was increased when variations became slight. Two measurements were done for each sample (along and perpendicular to grains). As no difference was observed between them, the average number was used for data treatments. The color variation was obtained using non-aged data as reference.

RESULTS AND DISCUSSION

UV/Visible Spectroscopy

The UV/Visible absorption spectra (Fig. 1-2) show that the metal oxides had a strong tendency to absorb UV radiation. Metal oxides seemed more efficient at the lowest wavelengths considered, whereas the light absorption was similar in the visible zone.

These results clearly show that the metal oxides had similar or better UV absorption properties in comparison to the organic stabilizers, especially at the lowest wavelengths.

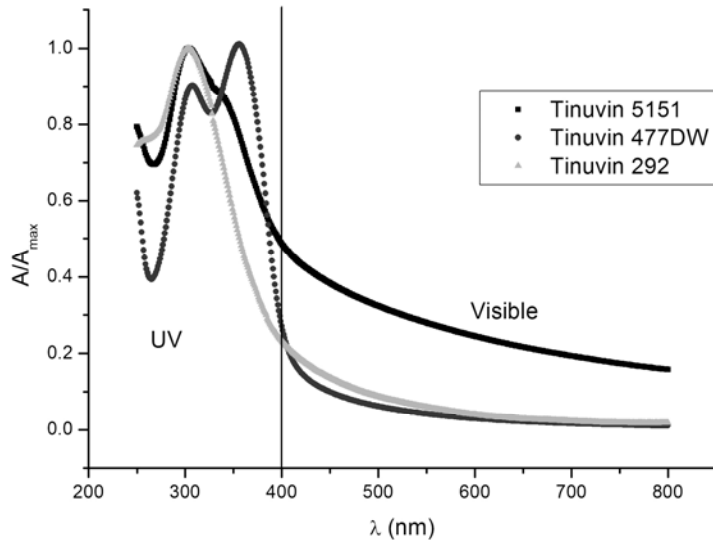


Fig. 1. Absorbance spectra for organic UV absorbers

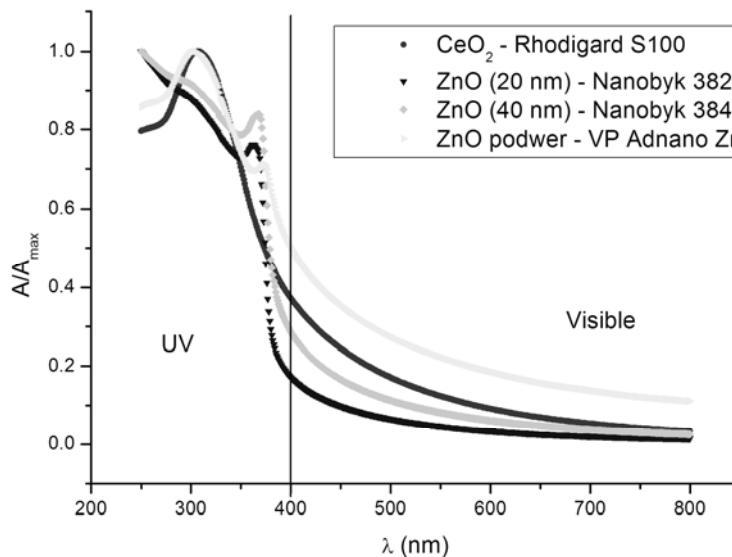


Fig. 2. Absorbance spectra for inorganic UV absorbers

Color Variation - Influence of the Type of Nanoparticles (pre-dispersed in water)

Accelerated aging had little influence on the lightness component of the maple wood (Fig. 3). Variations observed were below 2%. However, the organic products tended to lighten the color, whereas the metal oxides darkened it. Lightness can be understood as the net ability of the coating/wood to diffusely reflect light at low

temperature. This phenomenon is created by molecular relaxation processes (light scattering, fluorescence, and/or phosphorescence). The lightness could be directly influenced by UV absorbers properties that may absorb either a part of this energy (darkening) or release additional radiation at visible wavelengths (lightening). The difference of UV absorption between inorganic and organic stabilizers may explain the results observed (inorganic nanoparticles absorbing more UV radiation than organic ones).

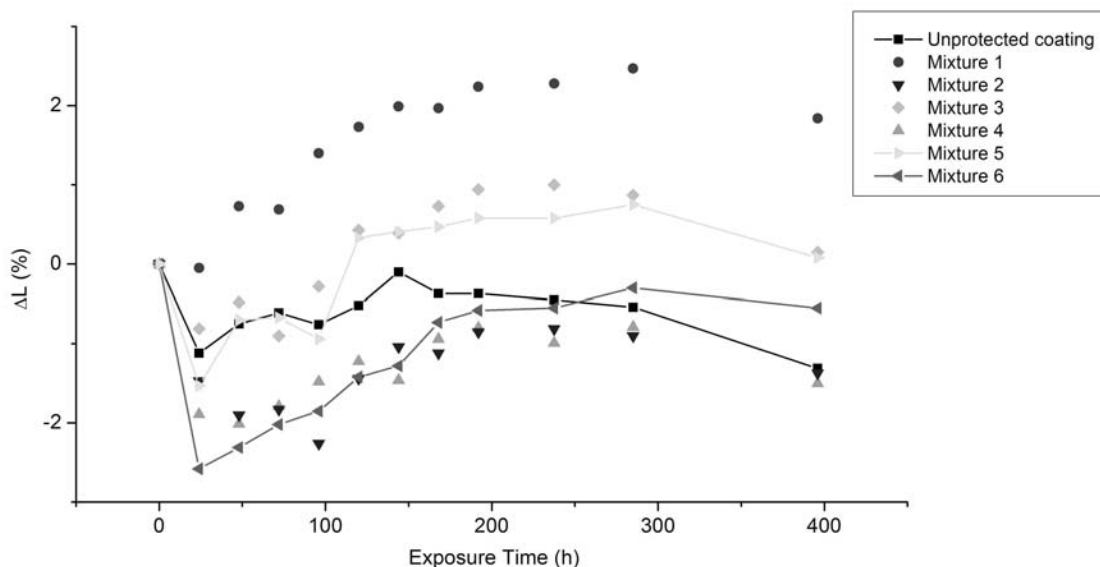


Fig. 3. Behavior of the lightness (ΔL) as a function of the exposure time for nanoparticles pre-dispersed in water with a concentration equal to 1 wt%

The green/red component slightly changed (less than 2%) with increasing exposure time (Fig. 4). As a general use, organic molecules changed the coating/wood color toward green. This result is in accordance with previous UV/visible studies, which show that the organic molecules absorb little in the zone corresponding to the green color (490-570 nm).

The color changes were mostly driven by yellowing (Fig. 5). Results show that organic absorbers gave the best protection in the short term, whereas inorganic ones were more efficient in the middle term. The yellowing was strongly reduced after 24, 48, and 65 hours of exposure (65, 48, and 41% decrease, respectively). On the opposite side, zinc and cerium oxides were relatively more efficient after 100 exposure hours, whereas the other stabilizers seemed to accentuate yellowing.

The nanoparticles' size seemed to be an important factor to reach a good protective efficiency (Fig. 5), though the results did not necessarily show an advantage for the lowest diameters. For instance, 40 nm zinc oxide nanoparticles were more efficient than 20 nm ones.

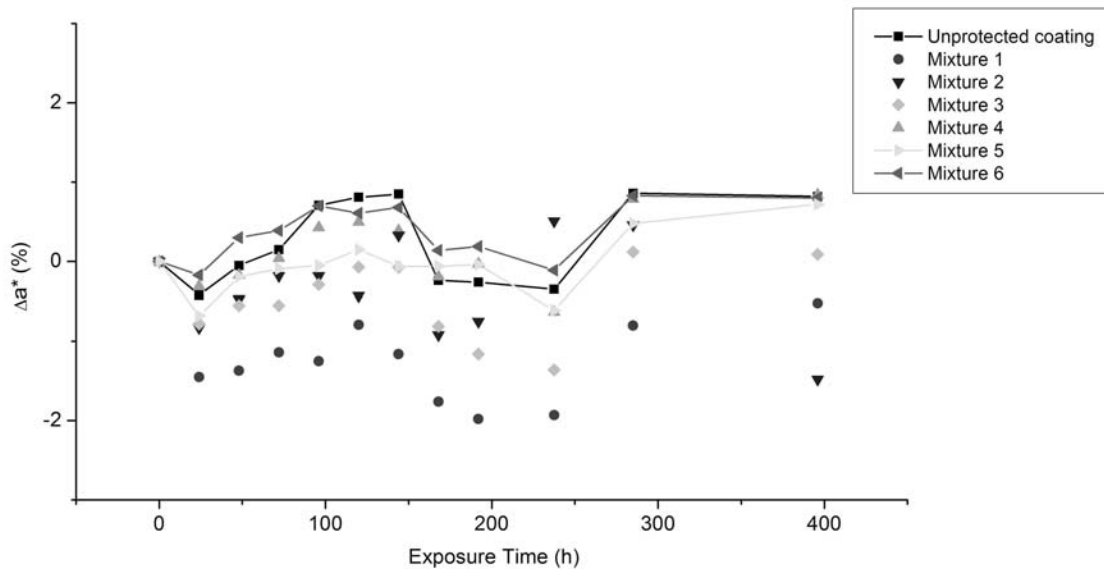


Fig. 4. Behavior of the red/green component (Δa^*) as a function of the exposure time for nanoparticles pre-dispersed in water with a concentration equal to 1 wt%

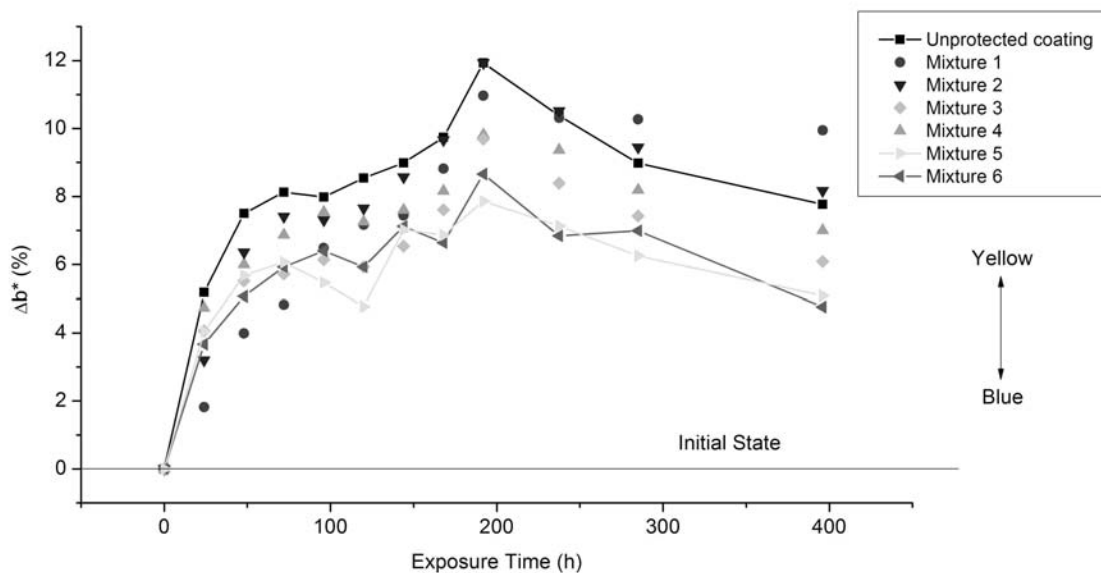


Fig. 5. Behavior of the yellow/blue component (Δb^*) as a function of the exposure time for nanoparticles pre-dispersed in water with a concentration equal to 1 wt%

Color Variation - Influence of Concentration and Nanoparticles Form (pre-dispersed or powder)

As noted previously, lightness was decreased in the presence of inorganic nanoparticles and increased in the presence of organic absorbers (Fig. 6). In addition, the specimens were darkened considerably when nanoparticles were added in powder form. It is likely that chemical products used to stabilize nanoparticles' suspensions reduce the absorption efficiency by a screening effect. Therefore, the UV absorption ability of zinc

oxides added in powder could be higher, which would explain this result. It follows that a strategy to use organic and inorganic UV absorbers together may supply better protection in the middle term (after 200 hours).

The concentration seemed to have a little influence (Fig. 7) on the green/red component, which changed little during the artificial aging (less than 2%).

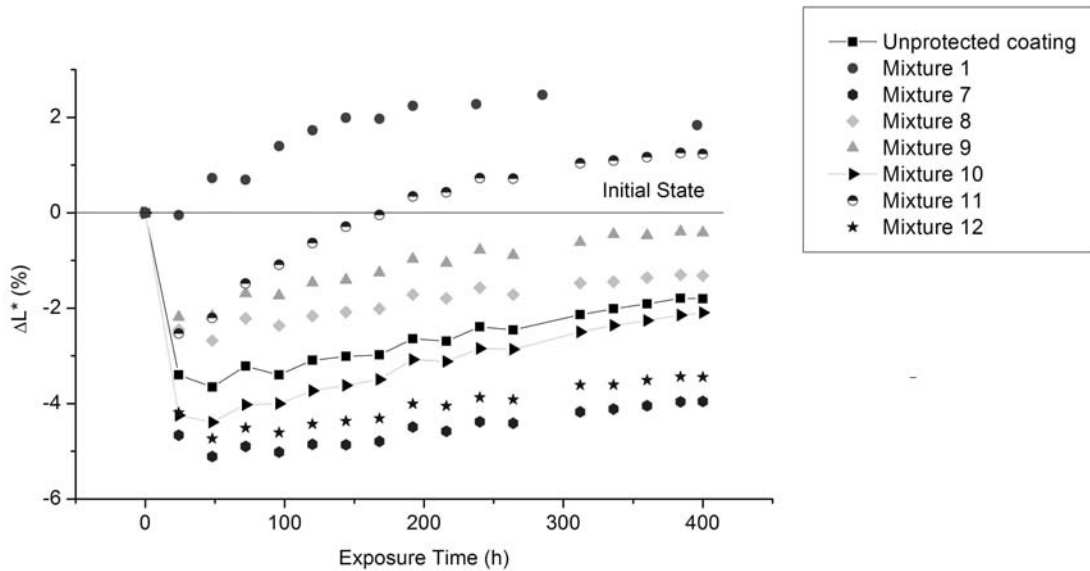


Fig. 6. Behavior of the lightness (ΔL^*) as a function of the exposure time for different mixtures and concentrations of nanoparticles in powder and pre-dispersed in water

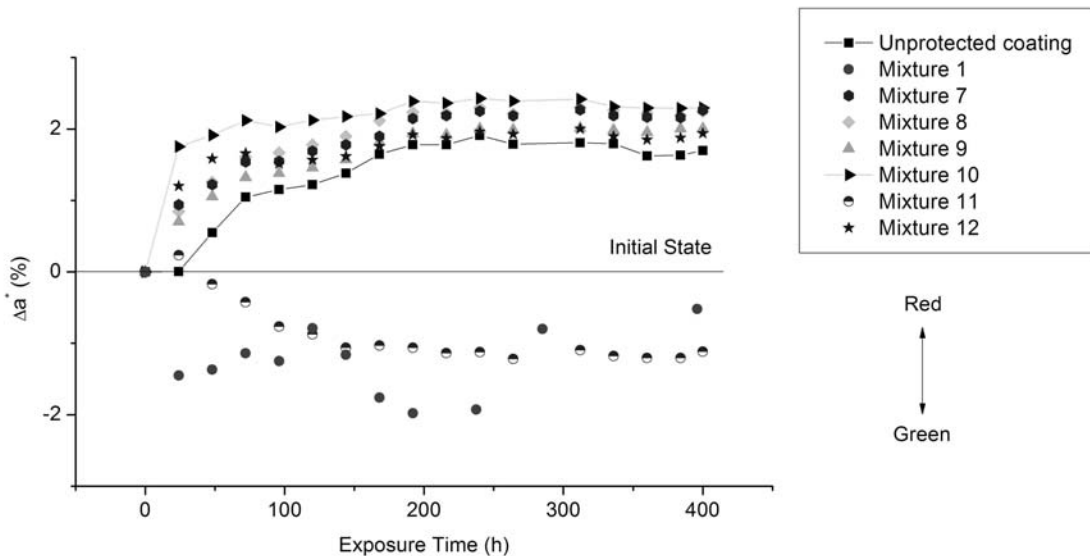


Fig. 7. Behavior of the red/green component (Δa^*) as a function of the exposure time for different mixtures and concentrations of nanoparticles in powder and pre-dispersed in water

As a general rule, the efficiency against yellowing was reduced with increasing concentration for powder systems (see ZnO 1% and 2% in Fig. 8). Indeed, nanoparticles tended to form aggregates at high concentration, and so decrease the ability of the particles to protect the coating. However, the results showed the opposite effect in spite

of the increasing tendency of the zinc oxide dispersions to aggregate (Fig.9). This result demonstrates it is not a necessary condition to have a full nanometric dispersion to obtain a good protection against UV radiation.

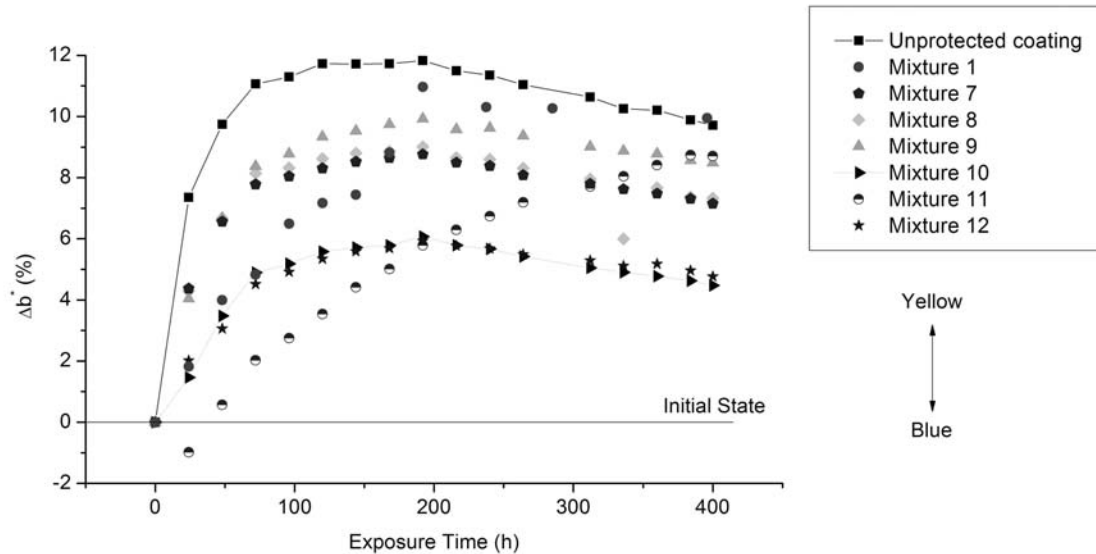


Fig. 8. Behavior of the yellow/blue component (Δb^*) as a function of the exposure time for different mixtures and concentrations of nanoparticles in powder and pre-dispersed in water

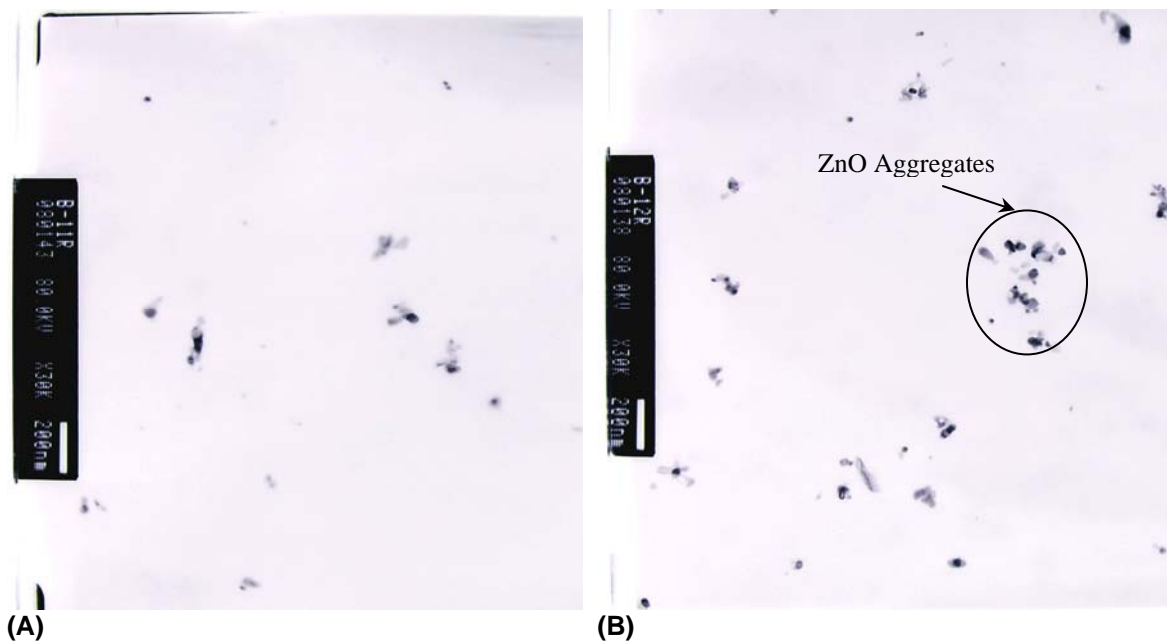


Fig. 9. Nanoparticle dispersions characterized by TEM at 30 kV - 1 wt% (A) and 2 wt% (B) zinc oxide in powder (VP Adnano ZnO 20)

On the other hand, it seems that the maximum of efficiency was reached with 1 wt% ZnO pre-dispersed nanoparticles (Fig. 5), because the same protection was obtained with 2 wt% (Fig. 8). This result may mean there is a critical concentration beyond which

the addition of nanoparticles will not have any influence on their effectiveness to protect a coating against UV radiation.

A good synergy was reached with the organic (Tinuvin 477 DW and 292) and inorganic (ZnO-40 nm) mixture. This strategy gave the best protection against yellowing until 200 hours. Thereafter, it stayed as one of the best until 300 hours. Migration and degradation mechanisms of organic UV absorbers may explain this drop in efficiency. However, inorganic nanoparticles may take over, and so allow maintenance of good UV resistance. Indeed, metal oxides may be sufficiently heavy to limit migration toward the surface and stable to avoid degradation by UV radiation in comparison to organic ones.

CONCLUSIONS

1. The efficiency of nanoparticles to stabilize wood's color over time was studied. Nanoparticles size, concentration, and form (powder or pre-dispersed in water) were shown to be important factors affecting the efficiency of the inorganic UV absorbers.
2. The nanoparticles' size was found to be important to reach the maximum of efficiency. Contrary to expectations, the efficiency did not linearly increase with decreasing nanoparticle diameter.
3. The pre-dispersed nanoparticles were less efficient than powder ones. One explanation is that chemical products used to stabilize the nanoparticles suspensions may have reduced their effectiveness by a screening effect.
4. For powder nanoparticles, concentration seemed to reduce the protective effect. SEM results showed increasing aggregation as the concentration was increased, which decreases the nanoparticles' ability to contribute to a protective coating. Moreover, the protective effect seemed to reach a maximum with concentration.
5. Finally, a synergy between organic and inorganic particles was found. This strategy gave the best protection against yellowing in the short term, and subsequently remained one of the best ones. Migration and degradation mechanisms of organic UV absorbers may explain this drop in efficiency. However, inorganic nanoparticles may take over, and so allow maintenance a good UV resistance. Metal oxides may be sufficiently heavy to limit migration phenomena.

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