

# Possibilities of Using Nanotechnology in Wood Colour Protection

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**Abstract**—Colourfastness characterizes a material's colour's resistance to fading or running. It is an important factor in the evaluation of wood, but unfortunately the colour of most wood species is not stable under outdoor conditions, it is mainly degraded by UV-radiation. The final result of outdoor weathering on unprotected wood surfaces is the well-known greying effect. To protect the colour of wood material, only surface protection is available nowadays, but in case of surface damages (scratching, cracks, etc.) this protection is not adequate. The impregnation of wood in the whole cross-section with UV-stable nanoparticles can protect the wood long lasting. Most promising results can be found in the literature about the utilization of TiO<sub>2</sub>, ZnO, CeO<sub>2</sub> and Fe<sub>3</sub>O<sub>2</sub> nanoparticles to protect the wood against UV-radiation. The advantage of using nanoparticles for wood protection against UV irradiation is that this treatment usually remains the initial colour of wood unchanged, or there is only a slight change in colour. This paper is a review of recent results and possibilities about the UV-protection of wood by nanoparticles.

## I. INTRODUCTION

The utilization of nanoparticles to improve the properties of wood is not widely investigated recently. On the other hand, many promising results were achieved with the use of nanoparticles in relation to the mechanical, combustion, hydrophobic and some other properties of different polymers, papers or textiles [1], [2],[3],[4],[5],[6],[7]. Recently, there is only limited information available about the utilization of nanoparticles to improve the wood properties, but all results are positive. With the use of different nanoparticles it is possible to reduce the moisture uptake, or improve UV-protection, mechanical properties and durability [8],[9],[10],[11]. In some cases fire resistance could be improved as well [12]. According to the careful examination of the results mentioned above, new ways of utilization in the field of wood science and technology are available. The novelty of the use of nanoparticles for the improvement of wood properties is that its effect is not known until now. Besides surface treatments a full cross-section treatment is possible which can make the service life of wooden products longer. The technical properties of most of the European wood species are in many respects behind some competing materials, which are originating from sources that are disadvantageous in aspect of sustainability (endangered tropical wood species, plastics). An important objective during the utilization of nanoparticles for UV-protection of wood is the expressive improvement of the properties of European wood species.

## II. COLOUR PROPERTIES OF WOOD

In the first approach, lightness can be used to characterize wood in colour. Colour variations on different effects can also be most clearly demonstrated by the change of lightness. However, colour cannot be specified with a single colour coordinate. The colour of the various wood species is broad enough in the yellow-red range (CIELab colour system), from the almost completely yellow to reddish shades ( $h_{ab} = 0 \sim 85^\circ$ ). Comparing the colour angle data with the lightness values, it can be concluded that there is a closer relationship between the two colour characteristics. The darker colour of the wood always has the shift towards the redder shades. Lighter wood species have yellowish hues. Saturation of the colour of wood embraces a much smaller range than lightness or hue, as it has low saturation. Among the main chemical components of wood, cellulose and hemicelluloses do not absorb visible light.

Natural lignin may contain quinoidal-structured chromophore groups as a result of build-up biochemical processes, but the colour is still pale yellow. The colour of the wood is, therefore, not determined by the main components, but by the extractive materials. Since the quality and quantity of extractive materials is significant to the tree species, the colour of the wood depends largely on the tree species. Substances are very sensitive to environmental impacts, especially light and heat, and therefore the colour of wood is influenced by environmental requisition. The moisture content also influences the colour of the wood. Sorption water changes the colour slightly to the fiber saturation point. Free water, however, results in a significant reduction of lightness. The lightness of green wood can be 10-15% lower than that of dry wood. Wet wood is better penetrated by light, and light absorption is higher. This change in the refractive index of the wood caused by moisture plays the leading role. The wood colour, to a small extent, is influenced by the surface roughness and the illuminating angles; these are the most important physical factors [13].

The wood has a complex anatomical structure. From this, visually perceptible segments of the early and late wood, the annual rings, the sapwood and the heartwood. It is possible to distinguish well the places called "false red heartwood" and other areas exposed to damages or disease. All of these play a significant role in the colour of the wood. The lightness of the early wood is greater than the late wood, which is determined by the loose structure and the difference in chemical composition. The standard deviation of the colour characteristics of homogeneous wood species (beech, mahogany) is smaller than that of less homogeneous species (poplar, oak, larch) [13]. The

colour difference can also be determined by objective colour measurement methods for trees that show visually distinction of the sapwood and the heartwood. The lightness of the heartwood is smaller and the colour shifts towards the reddish shades. The colour difference increases with drying. The reason for the colour difference is the polyphenol-type substances present in the heartwood, and the chemical transformation of polyphenols. Colour measurement can be used to determine the extent and the surface of the "false heartwood". The reason for the colour difference is in this case also a higher concentration of oxidized forms of polyphenols [13].

### III. COLOUR CHANGE OF WOOD

#### A. Effect of solar irradiation

The colour of the wood is predominantly determined by its chemical composition, primarily the extractives. However, lignin plays a significant role in colour change. The most powerful effects on the colour have polyphenols, hydrolysable and condensed tannins, stilbene derivatives, and lignols. But the terpenes and resins also affect the colour [14]. The colour of wood is significantly changed, if, by means of a suitable solvent or solvent system, extractives are extracted from the wood. Colour change is reflected in the increase of light, the shift of colour to yellow shades. The colour change of wood exposed to environmental impacts is most clearly determined by solar radiation and mainly by its UV range from climatic factors.

For photochemical processes it is necessary to absorb the light with corresponding energy (wavelength) of the chemical bonds of compounds involved in the construction of the material. The colour change resulting from the photochemical processes is thus determined by the nature, concentration and distribution of absorbing compounds, structures, functional groups (chromophores) as internal parameters, and by the wavelength and intensity of light, and the ambient atmosphere as an external factor [14].

Examining the wood as a combined system, it can be stated that a significant change in colour is applied to sunlight. Decrease of lightness has a significant effect on the colour shifting, changes in the hue have a smaller effect, and the smallest effect is the saturation. The rate of reduction of lightness in the initial stage of exposure to sunlight is fast and then decreases. After a long time of sunlight radiation, the wood changes colour in the opposite direction, a slow lightening starts. The phenomenon suggests consecutive processes. Photooxidation, the formation of colour compounds, is followed by the degradation of colour compounds by light. The decomposition of coloured compounds is also indicated by a relatively significant decrease in saturation with the slow increase in lightness. The effect can be increased by the leaching of dissolved compounds [14].

The important role of the wavelength of light is demonstrated by irradiation with light of different wavelengths that the colour of the wood may shift in a very different direction:

- 236 to 346 nm wavelengths change colour to yellowish shades

- 364 to 500 nm wavelengths change colour to reddish shades

Although the colour change is dependent on wavelengths and wood species, sunlight spectrum irradiation results in decisively reddish shades. As a result of the very large number of extractives in the different wood materials, the nature and extent of colour change depend on the wood species. However, a clear explanation for the causes of the changes can only be the light-induced reactions of the compounds present in the wood.

#### B. Effect of rain

Beside the solar radiation, the impact of water is the greatest in the degradation of wood. In contact with the surface of the wood, water is rapidly absorbed through the wood capillaries and then adsorption into the cell-walls begins. However, this process only takes place on the surface quickly; moisture penetrates much more slowly into the inner layers. As a result of this, the upper layers of the wood will swell while the volume of the inner layers remains unchanged. This results in tensions between the surface and inner layers of the wood. Tensile stresses exert on the surface layers, while compression stresses in the inner layers, causing the surface to crack [14].

Additionally, the role of water through surface leaching is significant during outdoor exposure. However, its effect has not been studied in detail such as UV radiation. Rain primarily enhances external degradation by washing out water-soluble extracts and degradation products of lignin and hemicelluloses from the surface. This results in the colour change of the exposed wood becoming faster and becoming gray. The presence of water also contributes to hydrolytic reactions during photodegradation, which also accelerates degradation of the surface during exposure [14]. It can also be shown that not only the liquid water (rain) but also the humidity of the air have an effect on the external degradation of wood. Higher humidity results in greater degradation [15].

#### C. Effect of heat

As a result of solar radiation, surface temperatures may increase significantly during outdoor use (50-70°C), which also promotes degradation. Although this temperature does not approach the glass transition temperature of lignin (130-150°C) or the heat degradation temperature of the wood components (160-260°C) [16]. Therefore, this temperature alone does not cause degradation of the surface, but it promotes photo oxidation and hydrolytic processes caused by light and water [17] [18].

### IV. COLOUR PROTECTION OF WOOD

The photoprotection of wood can be realized by absorbing or reflecting the damaging radiation.

#### A. UV-absorbers

UV absorbers absorb UV radiation, pass through tautomeric conversion and transform the energy of radiation into heat. A large number of UV absorbers are

available at present, such as benzophenone, benzotriazole, and triazine (Fig. 1.) [19]. The absorption characteristics of UV absorbers are determined by their chromophore group. Volatility and leaching resistance are dependent on molecular weight [20].

UV absorbers are widely used in coatings to protect against photodegradation. The effectiveness of the UV absorber can be increased by chemically bonding it to the surface to be protected. The most common use in this field is benzophenone or triazine UV absorbers with epoxy group. These UV absorbers can be bonded to the wood at high temperature in the presence of an amine catalyst. The protective effect is achieved through the protection of lignin on the exposed surface [21] [22] [23]. An alternative solution for the bonding of UV-absorbents to the surface of wood is the use of isocyanate-group containing UV absorbers [24]. UV absorbers provide effective protection against photodegradation of wood but their efficiency can be enhanced with compounds that neutralize free radicals that cause photo oxidation of wood [19].

### B. Radical scavengers

Several constituents such as phenolic antioxidants, heavy hydrocarbons and glycols, hindered amine light stabilizers are capable of neutralizing or blocking free radicals and some of them are used to protect wood from photodegradation [19]. Hindered amine light stabilizers are heat and light-proof derivatives of 2,2,6,6-tetramethyl piperidine. These compounds are capable of UV protection when combined with UV absorbers [19]. Hindered amine light stabilizers protect wood from photodegradation by terminating free radicals involved in photooxidation [25].

Hindered amine light stabilizers are available with different molecular weights and substituent groups (R1 and R2) (Fig. 2). The most important property, the free radical binding capability is determined by the R1 substituent group [20]. Hindered amine light stabilizers are also effective inhibitors of water degradation of wood [26].

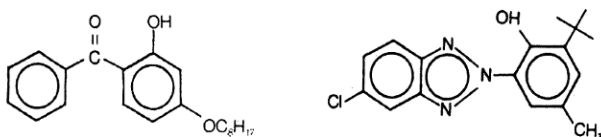


Figure 1. Chemical structures of typical benzophenone (a) and benzotriazole (b) UV absorbers used to photostabilisation of wood

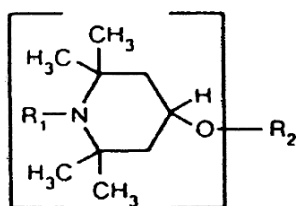


Figure 2. Example for the structure of a hindered amine light stabilizer (2,2,6,6-tetramethyl piperidine)

Hindered phenolic antioxidants serve to terminate free radicals generated by heat (Fig. 3.). Their effect is similar to the hindered amine light stabilizers, so they can be used to protect wood against UV degradation [27]. Against the hindered amine light stabilizers, these are non-regenerative and thus their concentration is constantly decreasing during application.

### C. Lignin modification

The wood material contains 20-30% of lignin, but it is unevenly distributed within the cell wall, so it can reach over 70% concentration in the middle lamella [28]. Lignin strongly absorbs UV light, creating aromatic free radicals resulting in depolymerization of the wood's polymers by sunlight. Lignin modification is an effective way to increase wood photostability [29]. Components suitable for lignin modification include: inorganic metal compounds, most notably chromic acid but also copper and cobalt chromates, ferric chloride and nitrate, and various manganese, titanium and zirconium compounds [29] [30] [31].

Chromic acid oxidizes the phenol groups of lignin, producing chromium (III) quinone complexes on the wood surface. Quinone and its derivatives are effective antioxidants and UV protectors. The protection is thus provided by stable ligninquinone complexes on the surface of the wood [32] [33]. Chromic acid significantly increases photostability of wood, reduces checking and surface erosion, increases dimensional stability and reduces hygroscopicity [29] [30] [34]. Trivalent chromium compounds are less toxic than chromic acid, but are also less effective in the protection against photodegradation [34].

Treating the surface of wood with oxidative manganese compounds such as manganese (III) acetate dihydrate or potassium permanganate is suitable for protecting wood from photodegradation. However, these compounds are less effective than chromium acids and stain the wood.

Titanates and zirconates are colourless and are also suitable for wood preservation against photodegradation. Titanates are more effective than zirconates, but the efficacy of both groups is less than that of chromic acid [31].

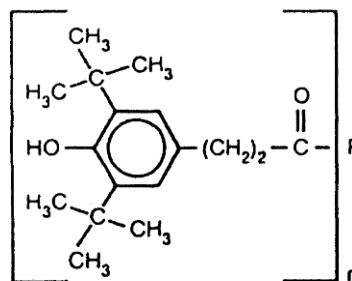


Figure 3. Example for the structure of a phenolic antioxidant

#### D. Surface coatings and penetrating finishes

The most common way of outdoor protection of wood against photodegradation is to use coatings such as paints, varnishes, stains and water repellents. The coatings can be divided into two groups: film-forming or penetrating. Film formers, such as paints, contain pigments that protect the wood from sunlight by blocking the surface of the wood. A common problem with film forming coatings is the loss of adhesion to the surface due to the cyclic dimensional changes in wood as a result of moisture changes. Due to the high maintenance requirements of the paints it is recommended to use penetrating coatings [13].

The penetrating coatings typically contain some hydrophobic, e.g. wax, oil or resin that penetrates into the wood and then cures. Contrary to film-formings, which form a barrier on the surface, water repellents form a hydrophobic surface to prevent water absorption through the capillaries [35]. The penetrating stains are water-repellent preservatives that contain pigments or UV stabilizers to protect the wood. Their failure is accelerated by the cracking of wood and the erosion of pigments from the surface. The deposition of air pollutants can also contribute to discolouration. Stains generally provide protection for 3 to 6 years depending on the wood species, wood surface texture and type and quantity of stain. Paints and stains change the colour of wood. In cases where it is necessary to preserve the original colour of the wood, clear film-forming finishes can also be used. Although they often contain UV stabilizers, they provide only moderate protection against outdoor exposure as they transmit sunlight and partly UV radiation. As a result of this, it is expected that the wood will be protected for a period of one to three years. Possible solution for increasing photostability with transparent coatings is the pre-treatment of wood with UV absorbers, hindered amine light stabilizers or chromic acid.

#### E. Pigments, nanoparticles

Due to the tighter environmental standards and a growing social demand, there is an increasing need for the use of environmentally friendly UV stabilizers. The main disadvantages of the compounds listed above are that they are in many cases toxic, carcinogenic. In contrast, the use of pigments and nanoparticles typically does not carry a significant environmental risk, especially compared to traditional solutions (e.g. chromic acid, UV absorbers, etc.). The use of pigments for UV protection has a decade-long history, but the application of nanoparticles has only spread over the past 5 to 10 years, and in most cases we cannot talk about industrial applications. However, based on the available test results, the rapid spread of the method can be expected, which is also indicated by the rapid growth of commercially available nanoparticle based UV protection products.

Basically, the smaller is the wavelength of the light, the greater is the ability to reflect it on small particles (Rayleigh-scattering). Accordingly, below a certain size, the particles are able to filter out the UV radiation, while they only have a small effect on the visible range of the spectra. This feature of small particles makes them suitable for photoprotection of wood. Most commonly, titanium dioxide, iron or zinc oxide particles are used as "transparent" photoprotection for wood. Clear synthetic

iron oxides are often used in paints. They differ from the iron oxide pigments because they are smaller in size (0,01-0,15  $\mu\text{m}$ ) and let pass the visible spectrum and filter the UV range. They are available as red, orange and yellow crystals. The desired UV filter effect can be achieved using a concentration of 2  $\text{g}/\text{m}^2$  or 2%. In addition, transparent iron oxide UV filters are able to maintain their protective effect during exposure to photodegradation over a longer period of time, as opposed to organic UV absorbers (e.g. benzotriazole) [13]. Iron oxides have a disadvantage of their colour, if necessary to preserve the original appearance of the wood.

Another option is to use micronized titanium dioxide or zinc oxide as a UV reflector for photoprotection of wood. Titanium dioxide is a highly effective white pigment for photoprotection that is used in opaque paints. Particles of titanium dioxide with few nanometers in diameter do not reflect visible light, but are able to protect the wood from the degrading effect of UV radiation. This effect can be achieved by titanium dioxide if it is in rutile form [35]. Titanium dioxide provides good protection for wood when applied at a concentration of 0,5-1%, possibly combined with iron oxide [37]. However, the concentration can be raised to up to 5% and thus efficiency without deteriorating the transparency of the surface film layer [38]. The transparency can be preserved optimally if the titanium dioxide particle size is between 2 and 50 nm. Titanium dioxide nanoparticles can be applied also directly on the wood surface by in-situ creating a thin layer on the surface. This allows the surface to withstand the damaging effect of UV radiation and also exhibits hydrophobic character. The hydrophobic nature prevents the surface from being cyclically wetted, thus protecting against surface cracks. It also protects against damaging organisms (e.g. mold) on the surface by reducing water absorption [39]. The disadvantage of the use of titanium dioxide nanoparticles is their UV-induced photoactivity which has a degrading effect on wood polymers and optionally on the carrier (paint) polymers [40].

In addition, micronized zinc oxide can be used to avoid photodegradation of wood. The advantage of using zinc oxide in spite of titanium dioxide is that the same UV filtering capability is available at lower concentrations and zinc oxide has less whitening effect on the surface. Nano zinc oxide can be applied directly to the wood as an aqueous dispersion, which provides good resistance to leaching to effectively protect the wood against sunlight over a longer period of time. Another advantage of zinc oxide is that it has bactericidal and fungicidal properties, which also contributes to reducing surface discolouration during outdoor exposure.

## V. CONCLUSIONS

Wood materials have a poor resistance to the damaging effect of UV radiation, and for this reason, long-lasting investigations have focused on colour retention procedures. Over time, there have been many solutions to preserving the colour of wood in outdoor use, but most of them do not provide long-term protection or are environmentally responsible for their application. This problem can be solved by nanoparticle based UV protection systems. They can be used as fillers in surface finishes (film forming or penetrating), or even directly as a

surface layer formed by an in-situ method on wood. Their further advantage is that they often produce a combined effect, not only against photodegradation, but also have a fungicide / biocidal effect or a water-repellent effect.

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