Colour stabilization of heat modified Norway spruce exposed to out-door conditions

O. Karlsson and T. Morén

Luleå University of Technology, Division of Wood Physics, Skeria 3, SE-931 87 Skellefteå, Sweden

ABSTRACT

Wood boards from Norway spruce (300 mmx125mmx10mm) were heat modified in a pilot chamber corresponding to Thermowood-D quality. The surface of boards was sprayed with diluted solutions of ferrous sulphate alone or in combination with subsequent spraying of a 30% solution of hydrogen peroxide. The boards were exposed to outdoor conditions during summer 2009 (45^o facing south). Colour coordinates were measured using a colorimeter.

Only small changes in colour of boards were observed directly after the surface treatments. Lightness increased for boards with no surface treatments during out-door exposure (seven weeks). Increase in lightness was delayed when ferrous sulphate was applied to the board. Lightness was essentially unchanged during the out-door exposure period when ferrous sulphate and hydrogen peroxide was used to modify the wood surface (at low hydrogen peroxide charge a small increase of lightness was, however, observed). Chroma decreased for boards with surface treatments but levelled out after a couple of weeks. On the other hand a decrease in chroma of boards with no surface treatments started after about four weeks exposure. Hue increased for all the boards until the fourth week. After that hue of untreated boards and boards treated with both ferrous sulphate and hydrogen peroxide continue to increase.

INTRODUCTION

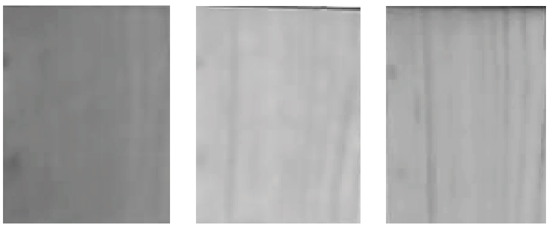
Heat modifying processes (such as Thermowood) could be characterized as a mild pyrolysis of the wood resulting in a reduction of hygroscopicity and increased dimensional stability. Although hardness of the product is increased a reduction in (surface) strength takes place during heat modification. The brownish colour formed by degradation reactions of wood components during heating is bleached on exposure to sun-light. Application of unpigmented or low-build stains and oils were found not to be able to give a weather stable coating (Jämsä et al. 2000). Lignin contributes to the colour of wood and if such structures and/or other colour giving groups could be stabilised it could reduce bleachability of heat modified wood surfaces towards sun-light. The UV-stability of lignin in wood was increased by blocking of phenolic groups with for example bensophenone groups (Kiguchi and Evans 1998) or by addition of UV-absorbers (Schaller and Rogez 2007). Increase in UV-stability of wood can also be performed by addition of ferric chloride and it is well known that increase in greying of wood can be done by addition of ferrous sulphate. However, the influence of the iron-salts on colour and stability of heat modified wood to out-door exposure is, at least to us, not known. In this paper we present results on stabilizing effect of ferrous sulphate and ferric chloride on surface of heat modified Norway spruce during exposure to out-door conditions. This was done by performing colour measurements with colorimeter. Importance of oxidation of wood surface by application of ferrous sulphate and hydrogen peroxide was also investigated.

EXPERIMENTAL

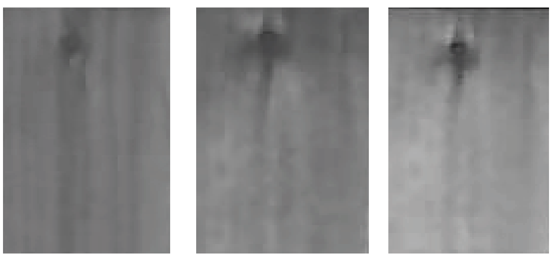
Wood from Norway spruce (sapwood side) were cut from a 25 mm thick board into 300x125x1.0 mm. Wood was heat modified in pilot chamber (Valutec) corresponding to Thermo-D properties and stored in-door at 20 ^oC. Before application of chemicals board surface was sanded. A 10% water-solution of ferrous sulphate ($FeSO_4x7H_2O$) was prepared by dissolving 10.3 g of the salt in 100 ml water (pH of the solution was 4.8). A 30% hydrogen peroxide solution was prepared by mixing 20 ml water with 25 ml of hydrogen peroxide (50%). About 10 mg of ferrous solution was sprayed on the surface of samples using a spray gun. A high (ca 50 mg) and a low (ca 10 mg) charge of hydrogen peroxide were applied to boards. The boards were dried in air and put out on a rack in 45^{o} tilt and facing south direction. Colour measurement was performed with a Minolta Chromameter CR 310 colorimeter before and when exposed to sunlight. Colour coordinates: Lightness (L), chroma (C) and hue (H) was measured. A decrease in chroma indicates a less saturated colour (grey) whereas a decrease in hue indicates (in this paper) a shift from red to yellow colour.

RESULTS

This paper presents results on colour (lightness) stabilisation of heat modified boards from spruce by addition of iron ion containing solutions with or without addition of hydrogen peroxide. Surface treated boards and boards with no surface treatment were put onto a rack in the summer of 2009. As could be expected considerable bleaching of the heat modified board surface took place within a couple of weeks. This is indicated in figure 1 showing the decrease in colour greying of the boards after out-door exposure. It is well known that a ferrous sulphate solution can be used to speed up greying of wooden surface, however, only a minor darkening of the heat modified board could be observed when the solution was applied to the board. On exposure to out-door conditions brightening of surface was substantially smaller for a board that had been treated with ferrous solution than a board that had not been surface treated (Fig. 1).



1a. 1b. 1c.



2a. 2b. 2c.

Figure 1. Effect of surface treatment with ferrous sulphate (2) or no surface treatment (1) on heat modified spruce wood. a. before exposure to outdoor conditions, b. after two weeks of exposure, c. after four weeks of exposure.

Analysis of colour coordinates during the first weeks of exposure to sun-light showed that lightness was essentially unchanged for boards that had been treated with the ferrous solution but increased for boards with no additions (Fig 2.). Lightness of the surface treated board started to increase when exposure was continued (Fig.2). A "delay" and increase in lightness was also observed with a board surface treated with Lewis acid catalyst, ferric chloride. Chroma decreased for the boards treated with ferrous solution whereas chroma was more slowly decreased for a board with no surface additives. Hue increased for both types of boards which mean that a shift towards yellow colour coordinate took place during the exposure. Increase for board treated ferrous sulphate, however, seemed to level-out at the end of exposure period

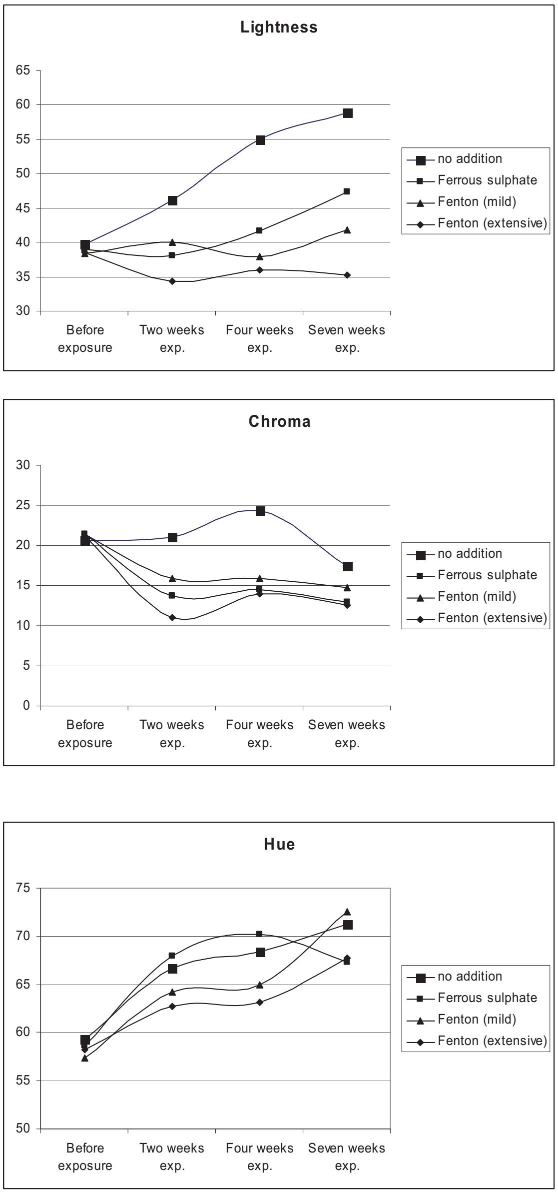


Figure 2. Colour measurements of heat modified boards exposed to sunlight. Effect of application of ferrous sulphate with or without hydrogen peroxide.

Ferrous sulphate is a mild reducing agent, however, when combined with hydrogen peroxide it forms a strong oxidising agent (also called Fenton's reagent) that has the ability to modify or introduce new chromophoric groups in the wood surface. Surprisingly, only small changes in colour coordinates could be observed for heat modified boards treated with Fenton's reagent. It can be seen in fig 2 that the lightness of oxidised surface was more stable than a board that had been treated with only the ferrous solution. After four weeks of exposure lightness, however, started to increase (Fig. 2). Decrease in chroma took place but levelled out after a few weeks. Hue increased during the exposure. The extent of surface activation was increased by addition of larger amounts of hydrogen peroxide and the typical formation of oxygen gas was observed. Still the colour of the board was not much altered by the extensive treatment and the measured lightness after seven weeks of exposure was essentially the same as before start of exposure (Fig.2). Hue was increased during the out-door exposure.

DISCUSSION

Lignin is brown in native state but deepen in colour in many industrial processes. Carbohydrates are more or less colourless but can form coloured compounds, by caramelisation reactions when heated. Detailed structure of chromophores in heat modified wood is still rather poorly described (González-Peña and Hale 2009). The chromophores generated during the heat modification of wood are not stable in sun-light and finally a greyish surface similar to weathered wood will appear. The retardation of bleaching of the board treated with ferrous solution in our experiments was quite unexpected. It is difficult to speculate on the reason for the retardation of bleaching based on the limited amount of experimental data but a few possibilities will be presented in the following sections.

During photodegradation of lignin radicals are formed and as ferrous ion has a reducing capability it may hinder further chain reactions of formed radicals. This does not mean that new chromophores are not formed during the exposure. The increase in hue and thus shift to more yellow colour in Fig. 2 points to that chromophores becomes modified during light exposure. Ferrous ion can also oxidise in air and this could be a reason why the lightness retardation of the treated boards was not stable and started to decrease after a couple of weeks.

Catechol (*ortho*-hydroxyphenols) structures can be involved in colour formation and may form during heat modification; an increase in phenolic content during heat modification by cleavage of beta aryl-ether bonds and methoxyl groups in lignin has been reported (Tjeerdesma 1998, Wikberg and Maunu 2004). Ferrous ion can form strong complex with catechols in lignin. One well known example is discoloration of tannin-rich heartwood of oak by ferrous ions. However, when ferrous solution was sprayed over the heat modified board only small differences in colour could be observed.

When ferrous sulphate was applied to an untreated wood surface a greying of the surface in the sun-light occurred only within a few days. Such a greying process was difficult to observe with the naked eye for the surface treated heat modified board. However, a decrease in the colour coordinate chroma was observed already in the beginning of the exposure for the surface treated boards (Fig. 2).

Fenton's reagent is a reactive and unselective oxidising system and reactive radicals can be formed when hydrogen peroxide is decomposed in presence of iron ions such as presented in figure 3.

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^{\cdot} + OH^{-}$$
$$Fe(III) + H_2O_2 \rightarrow Fe(II) + HOO^{\cdot -} + H^{+}$$

$$2\,H_2O_2 \rightarrow 2\,H_2O + O_2$$

Figure 3. Reactions of hydrogen peroxide in presence or Fe(II)/Fe(III) catalyst.

In presence of wood the radicals can react with wood components and introduce new functional groups instead of terminating into oxygen and water. This could involve formation of organic peroxides and radicals, hydroxylation of aromatic nuclei of lignin as well as further oxidation to quinones and acids. Surprisingly, lightness of the modified board after the oxidation with Fenton's reagent was affected only to a small extent. On the other hand, a darkening can be observed when untreated wood is oxidised with this reagent. It is, however, striking that lightness of heat modified board treated with the Fenton's reagent was essentially the same even after seven weeks of out-door exposure (Fig. 2). Hue increased, however, during out-door exposure (Fig. 2). This is an indication that the structure of chromophores in the surface oxidised board changes during exposure but that it still absorb light to a similar degree as before exposure.

Quinones are likely to be involved in the yellowing of paper but can under certain conditions have photo-stabilising properties. It has been proposed that weather stability of wood treated with strong oxidant chromic acid is due to formation of insoluble complexes with Cr (III) and quinones similar to the ones formed by chromic oxidation of guaiacol (Schmalzl et al. 2003). On the other hand, Evans and Schmalzl 1989 reported that a quinone-complex with relatively high solubility was formed when wood was treated with ferric chloride. In our experiments we found that treatment of wood with Lewis acid, ferric chloride led to a darkening but the lightness of the heat modified board started to increase in the end of the exposure period.

Quinones are not stable and could be oxidised further to acids that may form stable ferrous complexes. Also, heat modified carbohydrates can form strong complexes with ferrous ion (Benjakul et al. 2005, Natsuume and Ueda 1987). It is, however, questionable if such structures can really contribute directly to the colour stability of the oxidised heat modified board.

The current study was limited to a seven weeks period and gives only indications on the initial photo-degradation reactions of surface treatment of heat modified wood. The effect of prolonged exposure will be subject for further studied where also greying of the material will be focused in more detail. The effect of combination with oil surface treatments is also of interest as well as stability of potential chromophores in the process.

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