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SURFACE HARDNESS OF ORIENTAL BEECH PRE-IMPREGNATED WITH CCB BEFORE VARNISH COATING AFTER ACCELERATED LIGHTFASTNESS AND ACCELERATED AGING

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ABSTRACT

This study was designed to determine accelerated lightfastness and accelerated aging investigating the surface hardness performance of a polyurethane varnish (PV) and an alkyd based synthetic varnish (SV) coated Oriental beech (*Fagus orientalis* L.) wood that is pre-impregnated with CCB (chromium-copper-boron).

Results showed that while accelerated lightfastness hardened the wood surface, accelerated aging remarkably softened it. CCB pre-impregnation before varnish coating caused increase in hardness of coated Oriental beech wood after both exposure conditions. Higher concentrations of CCB resulted in harder surfaces of Oriental beech wood.

KEYWORDS: Surface hardness, Oriental beech wood, varnish, CCB, accelerated lightfastness, accelerated aging.

INTRODUCTION

Among the construction materials which are used by people wood hold a special place because of its impressive range of attractive properties, including low thermal extension, low density, and high enough mechanical strength (Bekhta and Niemz 2003). However, wood surfaces exposed outdoors are rapidly degraded because lignin strongly absorbs UV light, which leads to radical-induced depolymerisation of lignin and cellulose, the major structural constituents of wood (Evans et al. 1996, Derbyshire and Miller 1981). Changes in chemical, physical, and optical properties of wood lead to discoloration, loss of gloss, roughening of surface, and are also accompanied by alteration of mechanical properties of the three main components of wood-cellulose, hemicelluloses, and lignin appears to be oxidized and degraded by UV light more rapidly (Denes and Young 1999). Coatings can provide wooden materials with the desired aesthetical properties like color and gloss, but are mostly also of vital importance in the protection of wood against environmental influences like moisture, radiation, biological deterioration or damage from mechanical or chemical origin (De Meijer 2001). However, coating alone imparts to wood only superficial protection against some deteriorating agents for a limited time, often less than two years (Williams et al. 1996). Therefore, impregnation of wood with an appropriate water repellent or applying a varnish compatible preservative chemical prior to hazardous service conditions has been undertaken to make wood more stable against photochemical degradation, dimensional changes, biological composition, and fire (Williams et al. 1996, Wilkinson 1979). The most effective method of preventing the photodegradation of wood involves treatment with dilute aqueous solutions of inorganic salts, particularly hexavalent chromium compounds. Application of chromium trioxide to wood surfaces prevents lignin degradation during natural weathering (Kiguchi and Evans 1998, Evans et al. 1992) and predictably, when applied as a wood pretreatment, retards the deterioration of clear finishes and stains during exterior exposure (Feist 1987). Therefore, treatment of wood with a chromium-containing preservative such as copper-chromated-arsenate (CCA) before coating was suggested to extend the life time and durability of the coating system (Feist and Williams 1991, Bardage and Bjurman 1998). The chromium oxides in CCA, which bond to the wood after treatment, decrease photodegradation of the wood surface and can increase two-to threefold the durability of semitransparent stains (Williams et al. 1996). Since environmental awareness has forced the use of environmentally safe and arsenic free chemicals for wood and wood based composite protection (Evans 1995, Suzuki 1995), alternatives to arsenic containing preservatives are required. As a boron-containing wood preservative, which is generally considered to have low mammalian toxicity, chromium-copper-boron (CCB) was expected to fulfill this requirement (Yalinkilic et al. 1999a). Sell et al. (1974) studied outdoor performance of CCB treated on Obeche, red beech, spruce, and fir wood as surface treatment. High resistance of CCB-coated wood against weathering has been attributed to the protective effect of Cr-Cu-salt solutions on wood surface. Yalinkilic et al. (1999b) studied outdoor performances of a polyurethane varnish and alkyd-based synthetic varnish coated over chromium-copper-boron (CCB) impregnated Scots pine and chestnut. They reported that CCB pre-impregnation cause some loss in glossiness of the varnish layer coated on Scots pine but not that on chestnut. Feist (1979) and Feist and Hon (1984) reported that the application of aqueous solutions of chromium trioxide to wood surfaces had an inhibiting effect on the outdoor weathering process and enhanced the life of surface finishes applied over the treated wood. Feist and Williams (1991) studied unfinished and finished southern pine sapwood specimens treated with either CCA or chromium trioxide were exposed to accelerated weathering. They reported that small amounts of chromium salts on the wood surface greatly decreased weathering (erosion) of the wood caused by ultraviolet-light-catalyzed degradation.

This study was aimed to determine accelerated lightfastness and accelerated aging investigating the surface hardness performance of Oriental beech (*Fagus orientalis* L.) wood pre-impregnated with CCB before varnish coating.

MATERIAL AND METHODS

Preparation of test specimens and chemicals

Wood specimens of dimensions 10x100x150 mm (radial by tangential by longitudinal) were prepared from the air-dried sapwood of Oriental beech (*Fagus orientalis* L.) Aqueous solutions of CCB dissolved in distilled water were obtained in concentrations of 3 % and 9 %. CCB composed of 25 % boric acid, 36 % sodium bichromate, 37 % copper sulphate, and 2 % additives. Wood specimens were oven dried at 103 ± 2°C before and after treatment.

Impregnation method

Wood specimens were impregnated with aqueous solutions of CCB according to the ASTM D 1413-76 (1976). Retention was calculated by the following equation:

$$\text{Retention} = \frac{G\ .\ C}{V}\ .10\ \ (\text{kg.m}^{-3})$$

where: G - the amount of solution absorbed by the wood that is calculated from T_2-T_1,
T_2 - the weight of wood after impregnation (g),
T_1 - the weight of wood before impregnation (g),
C - the concentration of the solution as a percentage,
V - the volume of the specimen as cm^3.

Coating

An alkyd-based synthetic varnish (SV) and a polyurethane varnish (PV) of a two component type consisting of an aliphatic isocyanate-terminated component and an active hydrogen-bearing monomer, which when blended cures at room temperature with 4–5 h pot life of the blend was used. Alkyd- based synthetic and polyurethane varnishes were applied over untreated and CCB impregnated wood. To avoid potential interference in the surface characteristics of wood, filler was not used. Instead, varnish was applied as a primer coating for filling the voids and as a topcoat. Sufficient time for coat setting was allowed between successive applications. Specimens were left at ambient conditions for 24 h before the top coating according to the instructions given by the varnish manufacturer. Surfaces were gently sanded with abrasive paper to obtain a smooth surface prior to applying the topcoat.

Surface hardness

The surface hardness of test specimens was measured as the König hardness according to ASTM D 4366–95. Wood specimens were placed on the panel table, and a pendulum was placed on the panel surface. Then, the pendulum was deflected through 6° and released, at the same time, a stopwatch was started. The time for the amplitude to decrease from 6° to 3° was measured as König hardness.

Accelerated lightfastness test

Accelerated lightfastness was tested using UVA–340 lamps for the lightfastness performance of the wood. The wood specimens were exposed under the UVA-340 lamps directly and the temperature of the tester was 60 ± 2°C (Chang and Chou 2000). The total exposure time was 500 hours. Five replicates were made for each group.

Accelerated aging test

The accelerated aging test was performed according to the following exposure cycle period. This exposure cycle was mentioned to be a future work in (McNattand Link 1989):

Step	Exposure	Time (Hours)
1	Water soaking, 48.8°C	2
2	Dry air heating, 98.8°C	4
3	Water soaking, 48.8°C	2
4	Dry air heating, 98.8°C	16

The exposure cycle consisting of four steps was repeated for six times. Five replicates were made for each group.

RESULTS AND DISCUSSION

Surface hardness of Oriental beech wood after lightfastness exposure

Surface hardness properties of polyurethane and synthetic varnish coated Oriental beech wood that was pre-impregnated with CCB are given in Tab. 1 along with the retention values of the wood specimens.

Tab. 1: Surface hardness values of the Oriental beech wood after 500 hours of accelerated lightfastness exposure.

Chemicals and varnishes[a]	Concentration (%)	Retention ($kg.m^{-3}$)	Surface hardness				
			Before exposure		After exposure		Change (%)
			Mean[b]	SD[c]	Mean[b]	SD[c]	
PV	-	-	58.50	4.51	71.00	14.56	+21
SV	-	-	60.75	3.30	67.75	5.80	+11
CCB+ PV	3	9.29	62.25	8.18	79.25	15.90	+27
CCB+ PV	9	41.24	64.50	5.92	87.50	22.40	+35
CCB+ SV	3	9.29	62.50	12.34	76.25	16.20	+22
CCB+ SV	9	41.24	61.50	8.27	95.25	12.50	+54

[a] PV= Polyurethane varnish, SV= Synthetic varnish

[b] Results reflect the observations on the five replicate wood specimens.

[c] Standard deviation.

The retention values of the wood specimens were found to be 9.29 and 41.24 $kg.m^{-3}$ for pre-impregnation with 3 % and 9 % of CCB, respectively. The surface hardness values measured before accelerated lightfastness test were 58.50 and 60.75 for the polyurethane and the synthetic varnish coated wood, respectively. CCB pre-impregnation resulted in a slight increase in the surface hardness of the Oriental beech wood before exposure. All the coated and the treated wood surfaces hardened after 500 hours lightfastness exposure. Higher concentrations of CCB resulted in higher levels of surface hardness of the wood after exposure. The highest surface hardness values were measured for the Oriental beech wood after accelerated lightfastness test with 95.25 for the wood specimens pre-impregnated with 9 % CCB and then coated with synthetic varnish and 87.50 for the wood specimens pre-impregnated with 9 % CCB and then coated with polyurethane varnish. CCB pre-treatment had a contributory effect on the hardness of the coated wood after lightfastness test, since CCB pre-impregnation increased the surface hardness of wood coated with polyurethane from 11.6 to 23.2 and the surface hardness of synthetic varnish coated wood from 12.5 to 40.5 after accelerated lightfastness (Tab. 2). CCB pre-treatment resulted in more increase in the hardness of the synthetic varnish coated wood surface than that of the polyurethane varnish coated wood surface after exposure. The hardness of the alkyd coatings is a function of their formulations and can be improved with the additives, as they are compatible with many other resins. With variations in the formulations, it is also possible to obtain alkyd coatings with a wide range of properties (Seymour and Mark 1990, Kraft et al. 1967).

Surface hardness of Oriental beech wood after accelerated aging exposure

Tab. 3 shows the surface hardness of Oriental beech wood pre-impregnated with CCB before varnish coating before and after accelerated aging exposure. The retention values due to CCB impregnation of Oriental beech wood were 5.89 and 41.80 kg.m^{-3} for the treatments of 3 % and 9 % concentrations, respectively.

Tab. 2: CCB' increasing effect of surface hardness of Oriental beech wood after accelerated lightfastness exposure.

Chemicals and varnishes	Concentration (%)	Retention (kg.m^{-3})	Increase in surface hardness (%)
PV	-	-	-
SV	-	-	-
CCB+ PV	3	9.29	11.6
CCB+ PV	9	41.24	23.2
CCB+ SV	3	9.29	12.5
CCB+ SV	9	41.24	40.5

[a] PV= Polyurethane varnish, SV= Synthetic varnish

Tab. 3: Surface hardness values of Oriental beech wood after accelerated aging exposure.

Chemicals and varnishes[a]	Concentration (%)	Retention (kg.m^{-3})	Surface hardness				
			Before exposure		After exposure		Change (%)
			Mean[b]	SD[c]	Mean[b]	SD[c]	
PV	-	-	59.00	6.32	23.00	4.08	-61
SV	-	-	62.75	11.79	22.35	4.57	-64
CCB+ PV	3	5.89	63.75	10.50	29.75	5.12	-53
CCB+ PV	9	41.80	64.25	12.42	51.25	28.99	-20
CCB+ SV	3	5.89	60.50	2.38	34.50	10.38	-42
CCB+ SV	9	41.80	56.50	7.19	52.67	8.08	-6

[a] PV= Polyurethane varnish, SV= Synthetic varnish

[b] Results reflect the observations on the five replicate wood specimens.

[c] Standard deviation.

The surface hardness values measured before exposure were 59.00 and 62.75 for the polyurethane and the synthetic varnish coated wood, respectively. Our results indicated that the surface hardness values of both of the varnish coated wood surfaces drastically decreased after exposure. The surface hardness values measured after the exposure were 23.00 and 22.35 for the only polyurethane and the synthetic varnish coated wood, respectively. CCB pre-impregnation increased the surface hardness of the wood coated with polyurethane from 29.3 % up to 122.8 % and the surface hardness of the synthetic varnish coated wood from 54.3 % up to 135.6 % after the exposure (Tab. 4). Higher concentration levels of CCB resulted in higher surface hardness levels of the wood surface. Hansmann et al. (2006) investigated the artificial weathering of wood surfaces modified by melamine formaldehyde resins.

Tab. 4: CCB' increasing effect of surface hardness of Oriental beech wood after accelerated aging exposure.

Chemicals and varnishes	**Concentration (%)**	**Retention ($kg.m^{-3}$)**	**Increase in surface hardness (%)**
PV	-	-	-
SV	-	-	-
CCB+ PV	3	5.89	29.3
CCB+ PV	9	41.80	122.8
CCB+ SV	3	5.89	54.3
CCB+ SV	9	41.80	135.6

PV= Polyurethane varnish, SV= Synthetic varnish

They reported that the applied melamine treatment led to significant increases of surface hardness. Toker et al. (2009) studied the surface hardness characteristics of the Calabrian pine wood pre-impregnated with borates before varnish coating. They found that the borate pre-impregnation before varnish coating increased the surface hardness of wood surface. Baysal (2008) investigated the surface hardness properties of the wood pre-impregnated with CCB after 3 months of outdoor exposure. He found that the CCB pre-impregnation before varnish coating increased the surface hardness of the wood surface compared to the solely varnish coated wood surface. Our results are in good agreement with these researchers' findings. In another study, Yalinkilic et al. (1999b) studied the surface hardness properties of the polyurethane varnish and the synthetic varnish coated and over CCB-impregnated Scots pine wood and the chestnut wood after outdoor exposure. They reported that the coated wood surface became harder in time in response to outdoor exposure until a maximum hardness was reached followed by softening, whereas the uncoated surface softened steadily.

CONCLUSIONS

Surface hardness of the Oriental beech wood coated with a polyurethane varnish and an alkyd-based synthetic varnish, pre-impregnated with CCB was tested for accelerated lightfastness and accelerated aging exposure. While, the accelerated aging remarkably softened the coated and the impregnated wood, the accelerated lightfastness hardened it. CCB pre-impregnation caused remarkable increase in the surface hardness of wood specimens after both exposure tests, especially the accelerated aging exposure test. Higher concentrations of CCB resulted in higher surface hardness levels of the wood surface after exposure.

In conclusion, pre-impregnation of wood with CCB before varnish coating hardened the wood surface after both exposure tests. CCB was considered for pre-treatment as a chromium/ /copper/boron containing preservative in this study. Chromium in CCB was expected to protect the wood surface against weathering degradation, as boron and copper was expected to enhance the biological resistance of wood. Therefore, the bioactivity and the relatively high environmental safety of CCB-containing boron rather than the use of arsenic containing formulations has also attracted attention (Yalinkilic et al. 1999b).

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