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SURFACE CHARACTERISTICS OF CCA TREATED SCOTS PINE AFTER ACCELERATED WEATHERING

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ABSTRACT

Some surface characteristics such as surface hardness, gloss, and colour characteristics of wood treated with CCA (chromated copper arsenate) after accelerated weathering were investigated. Wood specimens were prepared from air-dried sapwood of Scots pine (*Pinus sylvestris* L.). Before tests, wood specimens were impregnated with 6.25, 12.50, and 25.00 percent aqueous solutions of CCA.

The results showed that CCA treatment caused increases in gloss and surface hardness of Scots pine after accelerated weathering. While the decrease in L^* values of Scots pine indicates that the specimens became darker, positive values of Δa^* and Δb^* indicate a tendency in wood surface to become reddish and yellow, respectively. Total changes in colour (ΔE^*) exhibited a systematic trend to higher values with increasing accelerated weathering time. ΔE^* of CCA treated Scots pine was lower than untreated Scots pine. Generally, surface characteristics of CCA treated Scots pine gave better results than untreated Scots pine after accelerated weathering.

KEYWORDS: Surface hardness, gloss, colour, Scots pine, CCA, accelerated weathering.

INTRODUCTION

Throughout the course of history wood has remained one of the most important renewable natural resources available to man. It is a natural, cellular, composite material of botanical origin-possesses unique structural and chemical characteristics that render it desirable for a broad variety of end uses. On the other hand, despite its versatility as a constructional material, wood is being superseded in several areas where other expensive materials such as metals, concrete, plastics, ceramics, etc. are emerging as preferred materials for use, even when the initial cost benefit favors the use of wood (Yalinkilic 2000). 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. 2002). The ultraviolet (UV) light portion of the solar radiation and the presence of moisture are the main causes for the weathering degradation of wood (Feist and Rowell 1982; Denes and Young 1999). Changes in chemical and optical properties belong to physical properties of wood lead to discolouration, 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). To date, 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 surface prevents lignin degradation during natural weathering (Kiguchi and Evans 1998; Feist 1979; Evans et al. 1992). Reactions of hexavalent chromium compounds with wood resulted in a wood surface enriched in chromium (III) bonded to components of the wood cell wall (Feist and Williams 1991). The presence of chromium (III) at the wood surface played a role in the observed resistance to weathering and in the protection from UV light (Williams and Feist 1984). CCA treated wood is widely used in outdoor architectural projects such as decks, walkways, gazebos and retaining walls (Feist and Williams 1991). Standard CCA solutions contain Cr in the form of CrO_3, As in the form of As_2O_5 and Cu in the form of CuO (Temiz et al. 2007). 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. 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). 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. Temiz et al. (2007) investigated colour changes of Scots pine impregnated with CCA, a metal-free propiconazol-based formulation, chitosan, furfuryl alcohol and linseed and tall oils after artificial weathering. They found that the colour changes were the lowest on CCA and linseed oil (full cell process) treated wood. Temiz et al. (2005) also investigated the colour characteristics of Scots pine impregnated with ammonium copper quat (ACQ and ACQ 2200), chromate copper arsenate (CCA), Tanalith – E 3491 and Wolmanit CX-8 after accelerated weathering test. They found that the most effective treatment for stabilizing wood colour was treatment with CCA and ACQ 1900. Chang et al. (1982) compared chromic acid treated and untreated southern pine following exposure to artificial UV radiation. The untreated specimens clearly show degradation of the middle lamella and cell wall. Chromic acid treated specimens show almost no degradation.

This study was designed to determine some surface characteristics such as surface hardness, gloss, and colour characteristics of CCA impregnated Scots pine after accelerated weathering.

MATERIAL AND METHODS

Preparation of test specimens and chemicals

Wood specimens measuring 6 x 75 x 150 mm were prepared from air-dried sapwood of Scots pine (*Pinus sylvestris* L.). Aqueous solutions of CCA were dissolved in distilled water to concentration 6.25, 12.50, and 25.00 percent. Wood specimens were oven dried at 103 ± 2°C before and after treatment.

Impregnation method

Wood specimens were impregnated with 6.25, 12.50, and 25.00 percent aqueous solutions of CCA according to ASTM D 1413-76 (1976). Retention of CCA was calculated from the following equation:

$$\text{Retention} = \frac{G \times C}{V} \times 10 \quad (\text{kg.m}^{-3}) \qquad (1)$$

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

Accelerated weathering test

Accelerated weathering experiment was performed in a QUV weathering tester with eight UVA 340 lamps. The weathering schedule involves a continuous light irradiation of 8 h following with a condensation for 4 h. The average irradiance was 0.89 $W.m^{-2}$ at 340 nm wavelengths. The temperature of the light irradiation period and the condensation period was 60°C and 50°C, respectively. Wood specimens were mounted on aluminium panels before placing in the QUV. The changes on wood specimens were monitored every 100 h for a total 500 h.

Surface hardness test

The surface hardness of test specimens was measured as the König hardness according to ASTM D 4366–95 (1995). 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. Five replications were made for each group.

Gloss test

The gloss values of wood specimens were determined according to ASTM D 523 (1970) with a measuring device (Micro-TRI-Gloss). The chosen geometry was an incidence angle of 60°. Results were based on a specular gloss value of 100, which relates to the perfect condition under identical illuminating and viewing conditions of a highly polished, plane, black glass surface. Five replications were made for each group.

Colour test

The colour parameters a^*, b^*, and L^* were determined by the CIE$L^*a^*b^*$ method. The L^* axis represents the lightness, whereas a^* and b^* are the chromaticity coordinates. The $+a^*$ and $-a^*$ parameters represent red and green, respectively. The $+b^*$ parameter represents yellow, whereas $-b^*$ represents blue. L^* can vary from 100 (white) to zero (black) (Zhang 2003). The colours of the specimens were measured by a colourimeter (X-Rite SP Series Spectrophotometer) before and after accelerated weathering. The measuring spot was adjusted to be equal or not more than one-third of the distance from the centre of this area to the receptor field stops. The colour difference, (ΔE^*) was determined for each wood as follows ASTM D 1536–58 T (1964):

$$\Delta a^* = a^*_f - a^*_i \qquad (2)$$

$$\Delta b^* = b^*_f - b^*_i \qquad (3)$$

$$\Delta L^* = L_f^* - L_i^* \quad (4)$$

$$(\Delta E^*) = [(\Delta a^*)^2 + (\Delta b^*)^2 + (\Delta L^*)^2]^{1/2} \quad (5)$$

where: Δa^*, Δb^*, and ΔL^* the changes between the initial and final interval values. Five replications were made for each group.

RESULTS AND DISCUSSION

Surface hardness

Surface hardness is given in Tab. 1 along with the retention of the Scots pine due to impregnated chemicals.

Tab. 1: Surface hardness of CCA treated Scot pine after accelerated weathering.

Chemicals	Conc. (%)	Retention (kg.m^{-3})	Before accelerated weathering	After accelerated weathering				
				100 h	200 h	300 h	400 h	500 h
Untreated	-	-	78.00 (4.97)	38.00 (4.76)	31.80 (1.10)	34.80 (3.90)	31.25 (8.26)	28.80 (4.66)
CCA	6.25	41.75	66.75 (14.36)	36.00 (9.87)	34.75 (4.32)	35.00 (6.99)	34.75 (7.61)	32.67(7.45)
	12.50	85.33	57.00 (6.81)	40.20 (7.01)	34.60 (4.75)	31.60 (3.14)	33.20 (2.42)	33.80 (4.79)
	25.00	128.62	48.83 (9.77)	41.40 (7.57)	32.17 (2.86)	25.40 (4.31)	31.20 (4.55)	36.80 (8.65)

Note: Values in parenthesis are standard deviations.

Retention values were calculated as 41.75 kg.m^{-3}, 85.33 kg.m^{-3}, and 128.62 kg.m^{-3} for 6.25, 12.50, and 25.00 percent of CCA treated Scots pine, respectively. Chromated copper arsenate (CCA) impregnation decreased surface hardness of wood surface compared to untreated Scots pine before accelerated weathering. However, CCA treatment had a contributory effect on the hardness of Scots pine specimens after 500 h accelerated weathering. For this reason, while the surface hardness was decreased approximately by 51 %, 40 %, and 24 % for 6.25, 12.50, and 25.00 percent of CCA treated Scots pine, respectively, it was decreased by 63 % for untreated Scots pine after 500 h accelerated weathering. Therefore, Scots pine wood impregnated with CCA could lead to the increases in surface hardness after accelerated weathering.

Gloss

Data for the specular gloss of the wood surfaces at a 60° incidence angle measured before and after exposure to accelerated weathering are given in Tab. 2.

While the highest gloss value was 4.36 for untreated Scots pine, the lowest gloss value was 2.15 for the 12.50 % CCA treated Scots pine before accelerated weathering. For this reason, chromated copper arsenate (CCA) impregnation limited the glossiness to a point in Scots pine before the exposure, possibly owing to the absorption and dispersion of the reflected rays by salt crystals prominent in the large lumens of the tracheids in the wide early wood sections of the grains. $HCrO_4^-$ ion in CCA solution is usually cited photoactivate.

Tab. 2: Gloss values of CCA treated Scots pine after accelerated weathering.

Chemicals	Conc. (%)	Retention ($kg.m^{-3}$)	Before accelerated weathering	After accelerated weathering				
				100 h	200 h	300 h	400 h	500 h
Untreated	-	-	4.36 (0.83)	3.43(0.12)	3.13(0.52)	3.13(0.35)	3.18(0.34)	3.16(0.29)
CCA	6.25	41.75	2.46 (0.31)	2.30(0.31)	2.43(0.30)	2.10(0.38)	2.70(0.39)	2.72(0.48)
	12.50	85.33	2.15 (0.17)	2.08(0.19)	2.00(0.20)	2.07(0.06)	1.98(0.22)	2.45(0.51)
	25.00	128.62	2.23 (0.34)	2.25(0.31)	2.30(0.35)	2.54(0.22)	1.90(0.18)	2.00(0.52)

Note: Values in parenthesis are standard deviations.

Thus, the presence of photoactive ion on the wood surface was assumed to cause some loss in glossiness of Scots pine. This result is consistent with the outdoor performance of CCB (chromated copper boron) impregnated Scot pine before varnish coating (Yalinkilic et al. 1999). While untreated Scots pine showed drastic gloss loss during the first 100 h accelerated weathering, it was not observed in all CCA treated Scots pine. Gloss loss values were approximately 21 % for control, while it was 6.5 % and 3.2 % for 6.25 and 12.50 percent of CCA treated Scots pine, respectively. Moreover, the gloss values of 25.00 percent of CCA treated Scots pine slightly increased after 100 h accelerated weathering. The gloss values of 6.25 and 12.50 percent of CCA treated Scots pine were increased after 500 h accelerated weathering, while it was decreased to some extent in 25.00 percent of CCA treated Scots pine. As a result, CCA impregnation decreased the gloss loss of Scots pine before accelerated weathering; however, it improved the gloss loss of Scots pine compared to untreated Scots pine after accelerated weathering as shown in Tab. 2.

Colour

Tab. 3 shows the overall changes in colour (ΔE^*) due to the accelerated weathering of the CCA treated and untreated Scots pine.

Tab. 3: Colour changes of CCA treated Scots pine after accelerated weathering.

Chemicals	Conc. (%)	Before accelerated weathering			After accelerated weathering																			
					100 h				200 h				300 h				400 h				500 h			
		L	a	b	ΔL^*	Δa^*	Δb^*	ΔE^*	ΔL^*	Δa^*	Δb^*	ΔE^*	ΔL^*	Δa^*	Δb^*	ΔE^*	ΔL^*	Δa^*	Δb^*	ΔE^*	ΔL^*	Δa^*	Δb^*	ΔE^*
Untreated		74.45	7.75	27.34	-7.88	5.72	11.19	14.84	-11.30	7.80	12.62	18.66	-13.53	8.65	10.93	19.45	- 14.79	8.93	10.36	20.16	-15.75	9.72	10.31	21.20
CCA	6.25	66.34	4.16	23.22	-1.43	3.03	8.40	9.12	-8.64	7.53	9.84	15.18	-10.64	8.70	10.21	17.18	- 12.83	9.25	8.36	17.97	-14.38	9.76	8.09	19.26
	12.50	63.81	3.50	22.31	-0.97	1.83	6.51	7.03	-8.23	6.39	7.83	13.09	- 10.28	7.60	8.33	15.33	-12.55	7.99	6.29	16.20	- 14.04	8.27	5.86	17.36
	25.00	60.92	2.60	21.80	-0.41	2.38	7.10	7.56	-6.88	6.72	9.50	13.55	- 10.25	7.96	8.37	15.48	-11.66	8.53	6.77	16.00	-13.11	8.84	5.97	16.97

In addition, changes in the individual ΔL^*, Δa^*, and Δb^* were also examined. The lowest values of ΔL^* that is the most sensitive parameter of the wood surface quality were obtained for the untreated Scots pine after all the accelerated weathering periods. The negative lightness stability (ΔL^*) values occurred during the accelerated weathering. Therefore, the wood surface got rougher and darker during the accelerated weathering (Grelier et al. 2000). Depolymerization of the lignin on the exposed surface may also render the surface darker (Temiz et al. 2005). The results showed that all the CCA treated Scots pine caused less changes in the lightness than untreated

Scots pine. Moreover, higher concentration levels of CCA resulted in lower ΔL^* values of Scots pine after each of the accelerated weathering periods. Positive values of Δa^* indicate a tendency of wood surface to become reddish. The Δa^* of weathered Scots pine was increased and became even more reddish. Δa^* of untreated Scots pine was rapidly increased after 100 and 200 h, followed by a slightly increased in other accelerated weathering periods. Positive values of Δb^* indicate a tendency of wood surface to become yellowish. During the first 100 h accelerated weathering exposure, Δb was sharply increased for all treated and untreated Scots pine. The results demonstrated that Δa and Δb^* of untreated and treated Scots pine had positive values after accelerated weathering. The increase in the chromaticity coordinate (Δa^*) and (Δb^*) may be explained by the modification of some chromophoric groups of lignin (Grelier et al. 2000). According to the results, Δa and Δb^* of CCA treated Scots pine were lower than untreated Scots pine after accelerated weathering periods. So, it can be concluded that CCA impregnation reduced reddish and yellow colours of Scots pine. The highest ΔE^* was observed on the untreated Scots pine during all the accelerated weathering periods. ΔE^* of CCA treated Scots pine was decreased to some extent. For this reason, the chromium in CCA formulation contributes to the stabilization of wood surface against UV light degradation (Temiz et al. 2005). The higher concentration levels of CCA resulted in lower ΔE^* of Scots pine. Moreover, ΔE^* showed a systematic trend to higher values with the increasing weathering time. Chromated copper arsenate (CCA) treatment demonstrated that the colour of wood surface was stabilized and not sensitive to UV light degradation. This can be attributed to the formation of complexes between chromium and quaiacyl units of lignin (Zhang and Kamdem 2000, Liu 1997, Pizzi 1980).

CONCLUSIONS

Surface hardness, gloss, and colour characteristics of CCA treated Scots pine after the accelerated weathering were investigated in the study. CCA impregnation was concluded to cause loss in gloss and to decrease the surface hardness of Scots pine. However, it increased the gloss and surface hardness of Scots pine after the accelerated weathering. Following the first 100 h of weathering period, surface hardness and gloss of untreated Scots pine were sharply decreased. The decrease in ΔL^* at all weathering periods indicated that the specimens became darker. The increase in the chromaticity coordinates, Δa^* and Δb^* for Scots pine indicated the yellowing and reddishness due to the accelerated weathering. The higher colour changes resulting from the accelerated weathering for untreated Scots pine were due to the higher contribution from the chromaticity coordinates, Δa^*, Δb^*, and ΔL^* (Tab. 3). Therefore, the contributions of chromaticity coordinates, Δa^*, Δb^*, and ΔL^* to overall colour changes in CCA treated wood during the accelerated weathering were found to be lower than untreated Scots pine. The results showed that the total colour changes (ΔE^*) in CCA treated Scots pine were lower than untreated Scots pine.

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