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Investigation of Color Difference in ACQ and CBHDO Treated Wood During Two-year Outdoor Exposure[1]

Jinah Lim[2] · Jung-Kwon Oh[3] · Jung-Pyo Hong[3] · Jun-Jae Lee[3,†]

ABSTRACT

In general, when wood products are used outdoors for a certain period of time the surface color of wood changes due to light, water, heat and so on. This color change can be considered importantly for the product's market value. In this study, the color change of ACQ (Alkaline Copper Quaternary) and CBHDO (CuO · H_3BO_3 · N-cyclohexyldiazenium-anion) treated wood and untreated wood was investigated during 2-year weathering test. From this experimental study, it was found that the colors of the treated wood changed more reddish and yellowish from green. Meanwhile, the untreated wood turned to grey color rapidly. Also, the color of the treated wood in short-term exposure changed closer to the inherent color of the fresh natural wood than that of the untreated woods.

Keywords : ACQ, CBHDO, color change, weathering

1. INTRODUCTION

Recently, with increase in the outdoor use of wood products, wood materials undergo degradation due to many deteriorating factors which can be classified into biological and non-biological agents. Biological agents lead to deterioration of wood more rapidly than that observed for non-biological agents (Scheffer 1971; Scheffer and Verrall 1973; Verrall 1963). Chemical treatment with preservative components has been mainly applied to enhance the biological resistance. The purpose of the treatment is to prevent decay caused by biological agents. It does not take into account the degradation induced by non-biological factors.

The constituents of wood are being degraded by various environmental factors including light, water, heat and so on, which is described as "weathering". Weathering is different from decay. Weathering results from the presence of environmental factors for an extended period of

1 Date Received July 18, 2014, Date Accepted November 21, 2014
2 Korea Forestry Promotion Institute, Timber Industry Support Team, Seoul 157-841, Korea
3 Department of Forest science, College of Agriculture and Life Science, Research Institute for Agriculture and Life Sciences, Seoul National University, Seoul 151-921, Korea
† Corresponding author : Jun-Jae Lee (e-mail: junaje@snu.ac.kr)

Table 1. Relative effect of various energy forms on wood

Form of energy	Indoors		Outdoors	
	Results	Degree of effects	Results	Degree of effects
Thermal				
Intense	Fire	Severe	Fire	Severe
Slight	Darkening of color	Slight	Darkening of color	Slight
Light*	Color change	Slight	Extensive color changes	Severe
			Chemical degradation (especially lignin)	Severe
Mechanical	Wear and tear	Slight	Wear and tear	Slight
			Wind erosion	Slight
			Surface roughening	Severe
			Defiberization	Severe
Chemical	Staining	Slight	Surface roughening	Severe
	Discoloration	Slight	Defiberization	Severe
	Color change	Slight	Selective leaching	Severe
			Color change	Severe
			Strength loss	Severe

Source : Stalker, 1971
* Both visible and ultraviolet light

time as shown in Table 1 (Feist and Hon 1984; Stalker 1971). Because of a limit of light penetration into wood (Browne 1957), the light weathering is influential up to a 2.5 mm thick surface layer and the erosion progresses slowly at, 5-12 mm per 100 year (Feist and Mraz 1978; Sandberg 1999). Factors which are the most influential to the surface of wood are light and moisture (Chang and Hon 1984; Feist and Hon 1992). The color change is firstly noticed on the surface of wood. Then, degradation of appearance, which is the result of weathering, is of supreme importance when the exterior uses of wood materials like siding, decking, railing are considered.

However, in order to use wood for outdoors, many researchers have focused on the study of prevention of wood damage by biological deterioration. CCA (Chromated copper arsenate) has been a major wood preservative for more than 50 years for many applications such as utility poles, children play grounds, building constructions, landscaping timbers, decks, fencing. However, there is an increasing public concern about environmental contamination from CCA treated wood (Temiz *et al*. 2005). On

January 2004, the U.S. Environmental Protection Agency (EPA) no longer allows pressure-treated wood containing CCA to be used. Because of the concern of environmental contamination and new regulations, ACQ (Ammoniacal Copper Quat) and CBHDO ($CuO \cdot H_3BO_3 \cdot$ N-cyclohexyldiazenium-anion) preservatives can be alternative choices for a replacement of CCA (Miyauchi *et al*. 2008).

Currently, several wood preservatives containing copper-amine are used. One of the potential problems of copper-amine-treated wood is the color stability. The surface color of copper-amine-treated wood changes from blue-green to gray-brown after a certain period time of outdoor exposure depending on the copper retention (Jin *et al*. 1991; Liu *et al*. 1994). Although it was reported that CCA-treated pine in exterior service undergoes a significant color change (Black and Mraz 1974), the mechanism of the change is not revealed clearly.

This study was to examine the ability of commercial preservatives to stabilize the color of the copper treated wood exposed outdoors.

2. MATERIALS and METHODS

2.1. Specimen processing and preservative treatment

Pitch pine (*Pinus rigida* Mill.) were used as specimens in this study. The logs were debarked and then round-processed into two different sizes of 140 mm and 160 mm in diameter by a rounding machine according to the previous study (Lim *et al*. 2011). Then, specimens have been cut in halves through the pith symmetrically. All of the specimens were trimmed into 2.4 m in length and kiln dried. After drying, the moisture content (MC) and specific gravity were measured by the oven-dry method (ASTM 1992; 2007). The moisture content was consistently 12.7 ± 0.4% and 13.3 ± 0.8% in 140 mm and 160 mm specimens and specific gravity was 0.42 ± 0.04 and 0.45 ± 0.03, respectively. The number of 140 mm and 160 mm in diameter specimens was 18 respectively, thus 36 specimens in total.

All specimens were divided into 3 groups by type of treatment. One and second groups were treated with the solutions of ACQ (Ammoniacal Copper Quat) and CBHDO ($CuO \cdot H_3BO_3 \cdot$ N-cyclohexyldiazenium-anion) respectively, according to the Korean guideline H3 grade. The third group are untreated specimens. To determine a preservative retention for each treated specimen, the treated specimens was tested, and the results were satisfied with the standard requirements for H3 grade (outdoor above ground service condition) as 5.99 kg/m^3 and 3.80 kg/m^3 for ACQ and CBHDO treatment. After the treatment, all of the three groups were then stacked for fixation in the laboratory for 6 weeks at room temperature.

2.2. Weathering test

The untreated and treated wood specimens were installed on posts as Fig. 1 shows. Each wood specimen was bolted to the posts in 2 m

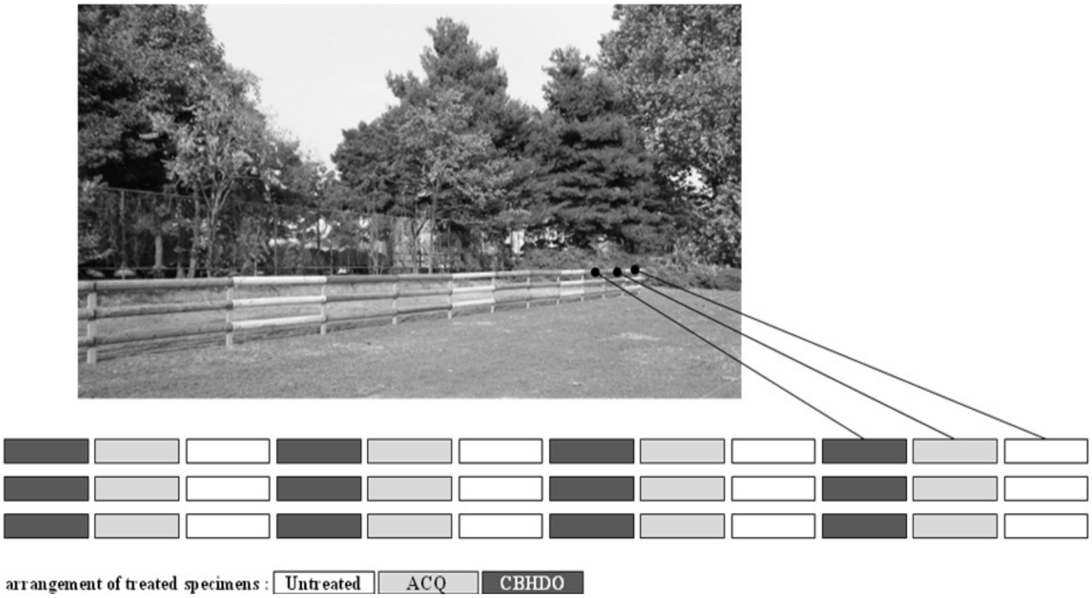

Fig. 1. The untreated and treated (ACQ and CBHDO) wood beams in the weathering test.

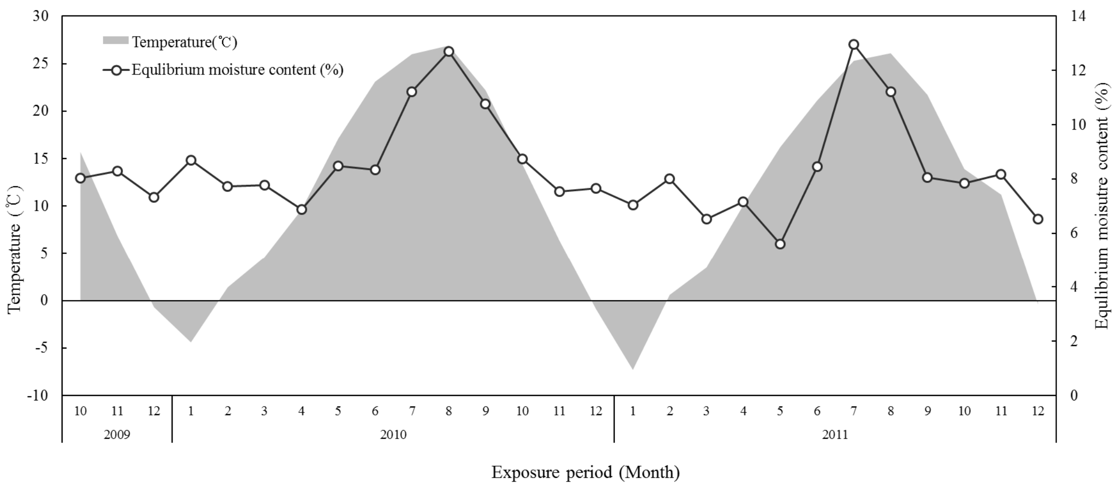

Fig. 2. Temperature and equilibrium moisture content of wood in Suwon, Korea during the observation period in the weathering test.

intervals. Three pieces of wood in a group were installed on two supporting posts at different heights. These wood beams were mounted alternately from the right in order of untreated, ACQ, CBHDO treated specimens (see Fig. 1). A round surface of the wood beam was faced

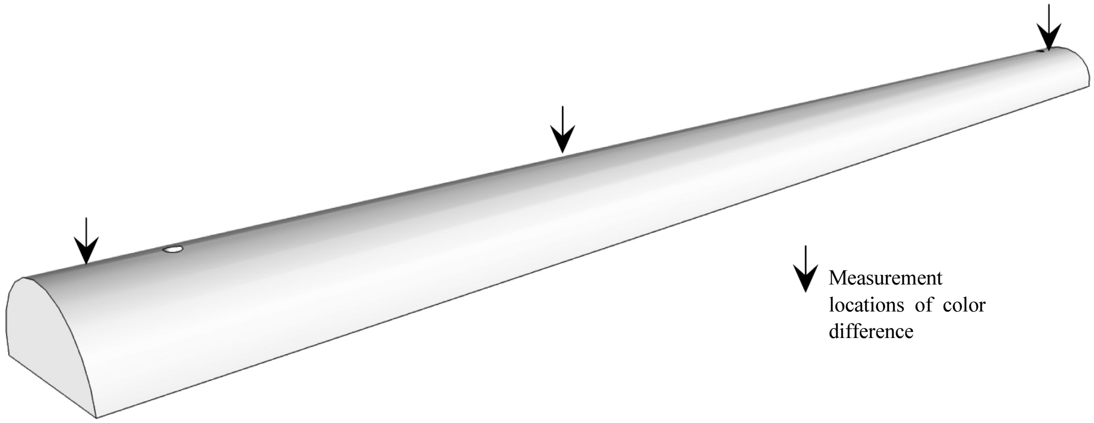

Fig. 3. Measurement locations of specimen.

to the south and a flat surface was faced to the north. The test field was located in Suwon, Korea (Lat 127°1′42N″, Long 37°15′46E″). The temperature and equilibrium moisture content (EMC) of this area was shown in Fig. 2. The weathering test started on November, 2009 and lasted for 24 months. The wood beam specimens were exposed to rainfall, sunlight and surrounding environment directly.

2.3. Color measurement

A surface color was measured by a spectrophotometer (CM-2500, Konica Minolta) at three locations on the surface of specimens as shown in Fig. 3. The surface color was evaluated according to the CIELab system (The Commission International de I'Eclairage) (ISO 1984) which describes a color by three coordinate parameters of L^*, a^* and b^*. L^* axis represents the lightness. a^* and b^* are the chromaticity coordinates: $+a^*$ for red, $-a^*$ for green, $+b^*$ for yellow and $-b^*$ for blue. The L^* varies for 0 (black) to 100 (white).

The color coordinates (L^*, a^* and b^*) for each specimens were measured at approximately 6 months interval during the weathering test. A color was measured on a color measurement devise using a D65 light source (SCI mode) established by the CIE 1976 (Billmeyer and Saltzman 1981). These measured values were used to calculate the color change ΔE^* as a function of the exposed period according to the following equations:

$$\Delta L^* = L_f^* - L_i^* \quad (1)$$

$$\Delta a^* = a_f^* - a_i^* \quad (2)$$

$$\Delta b^* = b_f^* - b_i^* \quad (3)$$

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (4)$$

ΔL^*, Δa^*, and Δb^* are the changes between the initial ($_i$) and the several interval values ($_f$). L^*, a^*, and b^* contribute to the color changes of ΔE^*. A low ΔE^* corresponds to a low color change or a stable color.

3. RESULTS and DISCUSSION

3.1 Changes of color on the surface of untreated and treated wood

Fig. 4 shows the readings of L^*, a^* and b^* at approximate six month interval measurements for two years. It shows that the treated wood has more green (lower a^*) and blue (lower b^*) color than those of the untreated wood. The surface colors of all three groups were changed more as the exposed time increases. The two treated woods have a similar tendency of color change.

At the beginning the untreated wood was brighter than the treated woods (see Fig. 1). However, as the weathering progressed, the wood surfaces of untreated wood became darker. As shown in Fig. 4(a), the brightness (L^*) of the untreated wood was decreased gradually. However, the treated woods showed a different tendency that the L^* increased as the elapse of exposed time get longer. Because of this opposite tendency, the brightness of the treated woods became quite similar to that of untreated wood after 24 months, even though the brightness of the wood specimens was significantly different at the beginning.

The a^* and b^* indicate the color of wood surfaces. The untreated wood specimens showed a larger change in color than that of the treated wood specimens in a year. In the beginning the untreated wood had more red and yellow color than those of the treated woods but, in the first 6 months the color changed a lot. In one year,

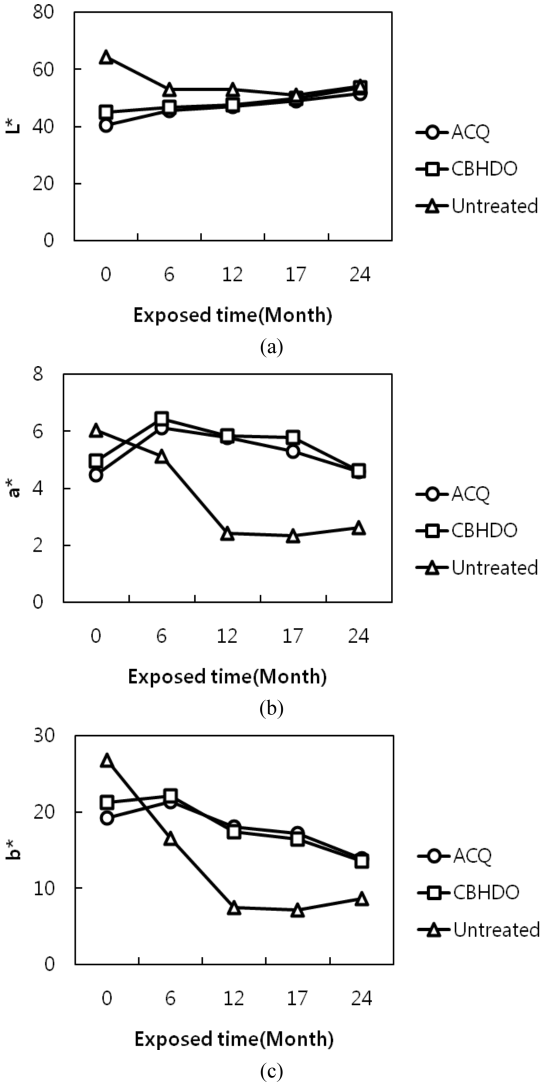

Fig. 4. Color changes in the weathering test (a) L^* value, (b) a^* value, (c) b^* value.

the value of untreated wood changed into a grey scale in which a^* and b^* were 2.41 and 7.47, respectively (If a^* and b^* are zero, it is grey). However, the color change of untreated wood became unnoticeable after one year of exposure. In case of the treated woods, a^* and

Table 2. Results of color stability

Exposure time (Month)	$\triangle E^*$		
	ACQ	CBHDO	Untreated
0-6	0.95	0.42	1.87
6-12	0.62	0.81	1.94
12-17	0.46	0.47	0.08
17-24	0.61	0.71	0.22
0-24	0.52	0.48	0.90

b^* increased for the first 6 months then, kept slowly decreasing until the end of 24-month test.

Because of the rapid color change of the untreated wood in the early stage, the color of the treated woods exposed for shorter than one year was more similar to the fresh natural wood than the untreated wood. The color coordinates also revealed that the a^* and b^* of treated wood in one year exposure were closer to those of the fresh untreated wood than those of the untreated wood. Moreover, the a^* of the untreated fresh wood has no significant difference from the treated woods which were exposed for the period between 6 months and 17 months (T-test, 95% significant level). The a^* indicates how close a color is to green or red. If the value of a^* for treated wood is close to the fresh untreated wood it means that the treated wood is no more green than a natural wood is. From these results, it was concluded that, in a short term exposure (6 months to 17 months), the color of the treated wood would become closer to that of fresh natural wood than the untreated woods, even though the initial color of the treated woods was very different from the fresh natural wood.

3.2. Color stability of untreated and treated wood

A stability of color was evaluated by calculating $\triangle E^*$ as shown in Table 2. Out of three groups, the untreated wood showed the highest $\triangle E^*$ for the whole experimental period. This means that the color of the untreated wood for the whole experimental period was unstable (0.90 for the untreated wood, 0.52 and 0.48 for ACQ and CBHDO treated wood, respectively). This result indicates that the treatments provide a higher color stabilizing effect. The beneficial effects of chromium can be attributed to the formation complexes between chromium and guaiacyl units of lignin (Feist and Hon 1984; Liu 1997; Pizzi 1980; Zhang *et al*. 2009). ACQ and CBHDO treatments slowed photo-degradation by retarding the formation of carbonyl groups. It was thought that the light resistance of both treated woods resulted from Cu (Ⅱ) chelating with functional groups in wood. The copper modifies the components in the cell wall so that the wood surface can have higher resistance to color change (Ozgenc *et al*. 2012). Compared to the untreated wood, a significant difference between the two treatments did not show (see Table 2). This is because both preservatives are based on copper (Jin *et al*. 1991; Liu *et al*. 1994).

4. CONCLUSION

In this study, the color change of ACQ and CBHDO treated wood for two year outdoor exposure was investigated. The surface colors of the treated woods were changed during the outdoor exposure. The two treated woods have a similar tendency in color change comparing with the untreated wood. From this experiment, we concluded the followings.

1. In an exposure period between 6 months and 17 months, the color of the treated wood changed closer to the inherent color of the fresh natural wood than that of the untreated woods. Especially, a^* (green or red) of treated wood did not show a significant difference from that of the fresh natural wood.
2. The untreated wood turned into grey color in a year.
3. Color stability of the treated woods was higher than that of the untreated wood. The preservatives may have an effect on the color stability.

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