J Wood Sci (2001) 47:228–232

ORIGINAL ARTICLE

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Protection and fastness of green color of moso bamboo (*Phyllostachys pubescens* Mazel) treated with chromium-based reagents

Received: January 21, 2000 / Accepted: June 12, 2000

Abstract The attractive green color of moso bamboo (*Phyllostachys pubescens* Mazel) culms fades without chemical treatment. Chromated copper arsenate (CCA) has been used to protect the green color of bamboo, but CCA is harmful to factory workers and the environment. To overcome the toxicity of arsenic in CCA, two chromium-based formulas developed by the authors, chromated copper phosphate (CCP) and chromated phosphate (CP), were evaluated for their protection of the green color of moso bamboo. The results revealed that bamboo treated with CP had a greener color than those treated with CCA or CCP. The concentration, treatment time, and CrO_3/H_3PO_4 ratio in CP solution greatly affected the color of moso bamboo culms. The attractive green color, which resembles the color of fresh-cut moso bamboo, was obtained by treating bamboo with 2% CP solution at 60°C for 3 h, using a 1:1 CrO_3/H_3PO_4 ratio in aqueous solution. In addition, the CP-treated moso bamboo exhibited excellent green color fastness in both accelerated ultraviolet lightfastness testing and outdoor weathering exposure.

Key words Moso bamboo · Green-color protection · Lightfastness · Weathering · Chromated copper phosphate (CCP) · Chromated phosphate (CP)

Introduction

People are drawn to bamboo for its green appearance. However, after drying or other preservation processing, the surface of bamboo turns from the original green color into gray and yellowish brown, losing this attractive characteristic. On the other hand, without protective treatment, bamboo culm is susceptible to attack by fungi and insects, which degrades its performance, shortens its service life, and reduces its value.

Developing a method to protect the green color of the bamboo culms could encourage the bamboo industry to explore the potential utilization and increase the economic value of bamboo products. Chemicals such as acid copper chromate (ACC), Tanalith C (CCA-type preservative), Boliden K-33 (CCA-type preservative), nickel nitrate, and copper sulfate have been evaluated for their effects on green-color protection and green-color fastness of bamboo culms.[1–4] Among these, Boliden K-33 has been demonstrated to be the most effective. Not only does it protect the green color on the culm surfaces, it also has good green color-fastness and weathering durability.[3,4] The arsenic component in Boliden K-33, however, has been recognized to be harmful to human health and to have an adverse impact on the environment. Hence, many countries such as Germany and Indonesia had restricted the use of this compound. To develop a chromium-based formula, the phosphoric component (belonging to the same VA group as arsenic in the periodic table) has successfully replaced the arsenic component in CCA.[5] Two formulas developed by the authors, chromated copper phosphate (CCP) and chromated phosphate (CP), have been proven to be effective green color protectors for ma bamboo (*Dendrocalamus latiflorus*), one of the most popular and valuable species in Taiwan. Furthermore, ma bamboo culms treated with CCP or CP exhibited excellent color fastness.[6]

Moso bamboo (*Phyllostachys pubescens* Mazel) is also an important economic species in Taiwan. It is used widely as a material for construction, furniture, and other handicraft works. No study of applying chromium-based, green-color protectors (CCP and CP) to moso bamboo has been done. There are also reports claiming that the effects of green-color protectors depend on the bamboo species.[2,7] Therefore, it is important to investigate the feasibility of CCP and CP green-color protectors for moso bamboo. The color durability and fastness of these chromium-based protectors for moso bamboo must also be studied.

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Materials and methods

Sample preparation

Three-year-old moso bamboo (*Phyllostachys pubescens* Mazel) culms were obtained from the forest of the Taiwan Forest Research Institute in Nan-Tou County. The bamboo culms were cut into 100mm (longitudinal) × 15mm (tangential) × 40mm (radial) pieces and stored at 4°C in the dark before experiment. Before treatment with the green-color protection reagents, the bamboo specimens were pretreated at 80°C with a mixture of 2% potassium hydroxide and 3% sodium lauryl sulfate for 30min. This pretreatment can remove waxes from the moso bamboo surface and provide better penetration and reaction for the subsequent green-color protection treatment. Five pretreated specimens were used for each of the following chemical treatments.

Chemical treatments

For evaluating the effect of chemical reagents on the green-color protection of moso bamboo, the alkali-pretreated specimens were treated at 60°C with various chemical reagents (listed in Table 1) for 6h. After rinsing the treated specimens with water, they were dried at 60°C for 12h.

Exposure test

For the color-fastness study, moso bamboo specimens treated with various green-color protecting reagents were exposed to two conditions. One was exposure to an artificially accelerated lightfastness tester, made by Q-Panel Co., using UVA-340 fluorescent UV lamps as a light source with the temperature of the black panel being 60°C. The UVA-340 fluorescent UV lamps produce a short-wavelength UV region between 365nm, a solar cutoff of 295nm, and peak emission at 340nm. The second condition was an outdoor weathering exposure with a rack. The weathering rack was positioned at a 45° angle to the ground on the campus of National Taiwan University and facing south. The weathering period was from January 1 to March 31, 1997. The average temperature was 16.8°C (range 7.0°–29.4°C), and the average relative humidity (RH) was 80%. The total duration of sunshine was 244.5h and the total precipitation duration was 421h, with a total precipitation of 360.7mm. After exposure for a designated time, the color differences were calculated and compared.

Color measurements

The color measurements were conducted using a Micro color meter color meter (Dr. Lange Co.). The light source was D_{65}, and the diameter of the measuring window was 10mm. Specimens were placed directly at the measuring window and the tristimulus values X, Y, and Z of the specimens were obtained directly from the colorimeter. According to TAPPI T524 om-79, the parameters of the CIE LAB color system were computed: L^* (the value on the white/black axis), a^* (the value on the red/green axis), b^* (the value on the blue/yellow axis), and ΔE^* (the color difference, $\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$). The a^* value is the best parameter to show the colors red and green. A positive a^* value indicated that the sample is red, and a negative value indicates a green sample. The smaller the a^*, the greener is the sample.

Analysis of variance

Duncan's test was employed to evaluate the differences of the chemical concentrations, each CP combination ratio, and the effect of the treatment times on the green color of moso bamboo culms. The measured color parameters were analyzed with 95% confidence levels.

Results and discussion

Green-color protection of moso bamboo

Moso bamboo can retain its greenish color after Boliden K-33 (belonging to the CCA family) treatment.[3] Because of the arsenic component, Boliden K-33 can cause harmful effects to humans and animals during processing. Research has pointed out that CCP or CP, chromium-based formulas, can protect the green color of ma bamboo,[5] but no study on the properties of moso bamboo treated with CCP or CP has been reported. In this study we evaluated the effectiveness

Table 1. Compositions of chemicals used

Chemicals[a]	Compositions	Ratios (w/w)	Concentration % (w/w)
CCA[b]	CrO_3, CuO, H_3AsO_4, H_2O	27:15:42:16	2, 5
CCP	CrO_3, $CuSO_4$, H_3PO_4	33:33:33	2
CCN	CrO_3, $CuSO_4$, HNO_3	33:33:33	2
CP	CrO_3, H_3PO_4	50:50	1, 2, 3, 5

CCA, chromated copper arsenate; CCP, chromated copper phosphate; CCN, chromated copper nitrate; CP, chromated phosphate

[a] All the chemical solutions were formulated in water

[b] Boliden K-33 (type B chromated copper arsenate) was used

Table 2. Changes in color parameters of moso bamboo culms after treatment with various chemicals at 60°C for 6 h

Chemicals[a]	CIE LAB		
	L^*	a^*	b^*
Fresh bamboo	40.9	−6.7	17.6
5% CCA(Boliden K-33)	46.0	−5.0	28.0
2% CCA(Boliden K-33)	42.6	1.8	24.2
2% CCN	47.1	6.6	30.3
2% CCP	43.9	−4.6	26.0
2% CP	48.5	−13.8	18.5

L^*, color parameter on the white/black axis; a^*, color parameter on the red/green axis; b^*, color parameter on the blue/yellow axis
[a] All the chemical solutions were formulated in water

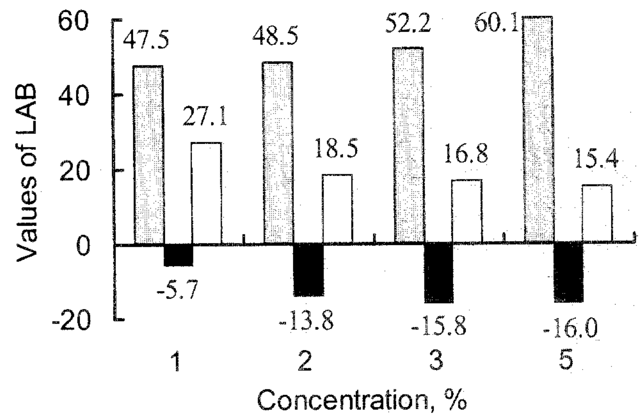

Fig. 1. Changes in the color parameters of moso bamboo culms after treatment with chromated phosphate (CP) of different concentrations at 60°C for 6 h. *Shaded bars*, L^* (color parameter on the black/white axis); *filled bars*, a^* (color parameter on the red/green axis); *open bars*, b^* (color parameter on the blue/yellow axis). *LAB*, CIE LAB color system

of CP and CCP on the green-color protection and fastness of moso bamboo. In addition to phosphate, nitrate (belonging to the same VA group in the periodic table) was used to replace arsenate for another green-color protecting formula, chromated copper nitrate (CCN).

Table 2 shows the changes in the color parameters of moso bamboo culms after treatment with various chemicals. Except for the specimens treated with 2% CCA (Boliden K-33) and 2% CCN, the a^* values of moso bamboo culms treated with all the other reagents were negative. The bamboo culms treated with 2% CCA and 2% CCN were yellowish brown. It is clear that 2% CCN or 2% CCA treatment cannot offer green-color protection to moso bamboo culms. When moso bamboo was treated with 5% CCA or 2% CCP, the a^* values of both specimens (−5.0 and −4.6, respectively) were slightly higher than that of fresh bamboo culm (−6.7). These two treated moso bamboo culms were yellowish green by visual examination. Furthermore, the color parameters of 2% CP-treated moso bamboo were 48.5 (L^*), −13.8 (a^*), and 18.5 (b^*), indicating that its color was not only greener but brighter. Hence, moso bamboo treated with 2% CP have a more attractive emerald-green color.

Table 2 also shows that different colors were observed on moso bamboo when they were treated with two different concentrations of CCA solution. Four concentrations of the CP solution were examined for color protection, and the results are shown in Fig. 1. The L^* value of CP-treated moso bamboo culm increased, whereas the a^* and b^* values decreased, with increasing concentrations of CP solution. The statistical analysis also shows that there is a significant difference in the color parameters of bamboo treated with various concentrations. When 1% CP was used, the L^*, a^*, and b^* values were 47.5, −5.7, and 27.1, respectively; the color parameters of specimens treated with 5% CP were 60.1, −16.0, and 15.4, respectively. It means that the color of moso bamboo culm becomes brighter and greener with the increase in CP concentration. On the other hand, visual examination of 5% and 3% CP-treated moso bamboo culms disclosed that some bamboo epidermis was peeled off and could not retain a uniform surface. The peel-off side effect was not observed in 1% or 2% CP-treated bamboo culms. We concluded that 2% CP concentration is the best green-color protection reagent for moso bamboo.

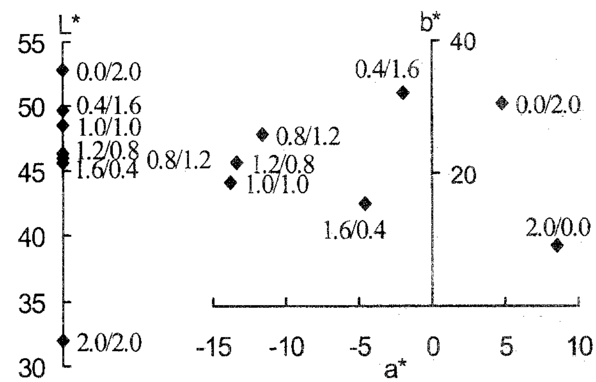

Fig. 2. Influence of CrO_3/H_3PO_4 ratios in 2% CP on the color of moso bamboo culms being treated at 60°C for 6 h. The *numbers* in the plot are the CrO_3/H_3PO_4 ratios

Both CrO_3 and H_3PO_4 are key components in the CP solution to conserve the green color of bamboo culms.[5] Various CrO_3/H_3PO_4 ratios were examined to explore the most appropriate composition of CP. The results, shown in Fig. 2, revealed that the a^* values of bamboo culms decreased first and then increased with the increasing CrO_3/H_3PO_4 ratio. When the CrO_3/H_3PO_4 ratio was 1:1, the a^* value of the specimen was the smallest (−13.8), and its L^* value was 48.5. It was shown that the a^* value decreased from 8.5 to −4.5 when the CrO_3/H_3PO_4 ratio changed from 2:0 to 1.6:0.4. On the other hand, the a^* value increased from −11.6 to −2.0 and the b^* value increased from 25.7 to 32.1 when the ratio was changed from 0.8:1.2 to 0.4:1.6. The differences in the color parameters among these various CrO_3/H_3PO_4 ratios are statistically significant. These results demonstrated that the ratio of these two chemicals greatly affected the color of moso bamboo culms. Among the ratios used, the color of moso bamboo culms was greenest when the CrO_3/H_3PO_4 ratio was 1:1. It was also noted that the color of treated bamboo was quite close to that of

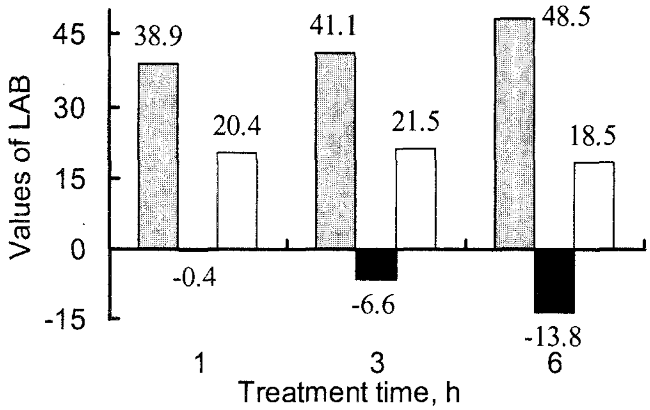

Fig. 3. Changes in the color parameters of moso bamboo culms after treatment with 2% CP at 60°C for different times. See Fig. 1 for explanation of bars

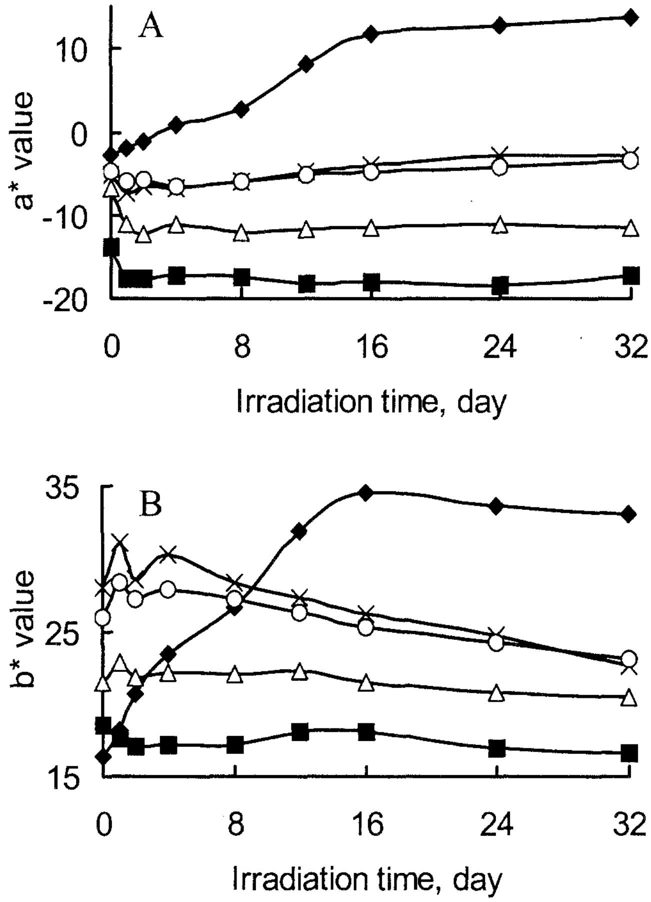

Fig. 4. Changes in a^* value (**A**) and b^* value (**B**) of moso bamboo culms treated with chemicals after lightfastness test for 32 days. (*Diamonds*, untreated; *squares*, 2% CP, 6h; *triangles*, 2% CP, 3h; ×, 5% chromated copper arsenate (CCA); *circles*, 2% chromated copper phosphate (CCP)

fresh bamboo specimens when the ratio was 1.6:0.4. In terms of taking the economy of commercial production into consideration, however, the 1:1 CrO_3/H_3PO_4 ratio was the better choice for producing bamboo with a greener color.

Considering the practical application for manufacturing green bamboo products, it is also important to reduce the treatment time during the manufacturing process. The color protection was studied with three treatment times (1, 3, and 6h) in 2% CP solution. Figure 3 shows that the a^* values were −0.4, −6.6, and −13.8 and the L^* values were 38.9, 41.1 and 48.5, for 1, 3, and 6h of treatment, respectively. These differences caused by the treatment times are statistically significant. It was noted that the color parameters (L^* 41.1, a^* −6.6, b^* 21.5) of moso bamboo culm treated for 3h were close to those of fresh bamboo culm (L^* 40.9, a^* −6.7, b^* 17.6), with a slight color difference (ΔE^* 3.9). Hence, choosing the proper treatment time with an appropriate green-color protector generated a green color close to that of fresh bamboo culm. With regard to the mechanisms for the green-color protection of bamboo after treatment with chromium-based reagents, further studies are in progress and the results will be reported in the near future.

Green color fastness of moso bamboo

Two exposure tests, the accelerated UV light fastness test and the outdoor weathering test, were used to study the green-color fastness and durability of moso bamboo treated with various green-color protectors. The results of accelerated UV light fastness are displayed in Fig. 4. After 32 days of the light-fastness test, the a^* and b^* values of untreated moso bamboo increased from −2.5 and 16.4 to 13.8 and 33.1, respectively. In other words, the color of the specimen changed from green to yellow during the 32-day light-fastness test. The a^* values of 5% CCA-treated bamboo culms and 2% CCP-treated culms changed from −5.0 and −4.6 to −2.6 and −3.2, and their b^* values changed from 28.0 and 26.0 to 22.7 and 23.1, respectively. The a^* values of 5% CCA-treated and 2% CCP-treated specimens did not increase significantly after 32 days of lightfastness, but their color did change from a vivid yellowish green to a dull brownish green. The a^* values of bamboo treated with 2% CP for 3 or 6h decreased during the first 2 days after irradiation and then retained their green color during the next 30 days; but there were only slight decreases in b^* values of both specimens. Their b^* value differences, which were obtained by subtracting the b^* values of nonirradiated specimens from those at 32 days of irradiation, were less than −1.9. Compared with the color changes of CCA- or CCP-treated bamboo, it was clear that the green-color fastness of CP-treated moso bamboo was excellent. The cause of the decrease in the a^* value during the first 2 days after irradiation may be photoactivation of the reagents before the fixation, subsequently followed by the migration and precipitation of chemical products to the surface of specimens. Similar results have been reported on CCA-treated wood[8] and CrO_3-treated ma bamboo.[6]

Variations in the a^* and b^* values of the specimens after exposure to the outdoor environment for 12 weeks are shown in Fig. 5. Similar to the results obtained from the accelerated UV light-fastness test, untreated moso bamboo

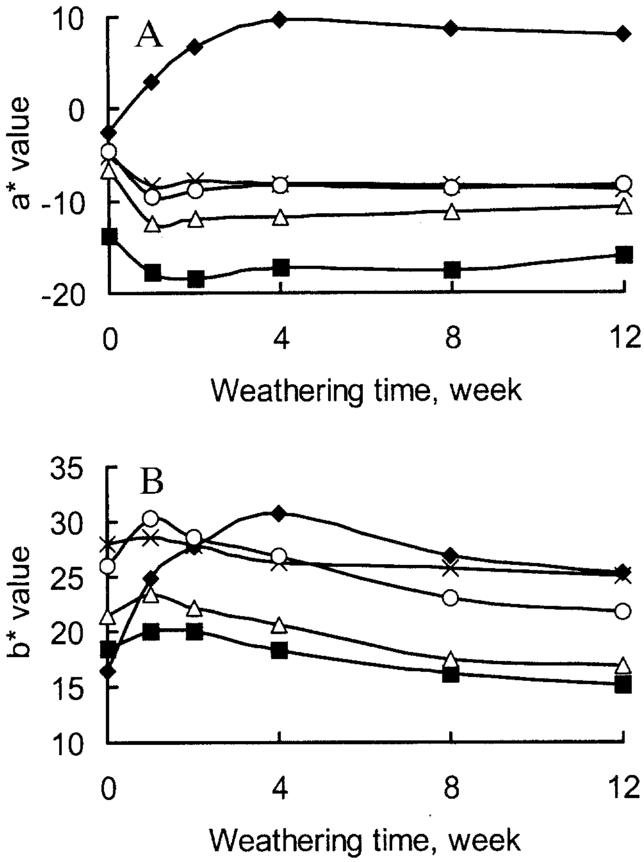

Fig. 5. Changes in *a** value (**A**) and *b** value (**B**) of moso bamboo culms treated with chemicals after a weathering test for 12 weeks. See Fig. 4 for explanation of symbols

culm turned from green to yellow. The *a** and *b** values of the specimen exposed to outdoor weathering for 12 weeks were 8.0 and 25.3, respectively. The *a** values of moso bamboo culms treated with chromium-based reagents decreased during the incipient stage of weathering and retained their *a** values during the 12 weeks of weathering exposure. Their *b** values all decreased after 12 weeks of weathering. At 12 weeks of exposure their *a** and *b** value differences, obtaining by subtracting their *a** and *b** values at 12 weeks of exposure from those of unexposed specimens, ranged from −2.2 to −4.2 and from −3.0 to −4.6, respectively. They all became greener and did not show any yellowing phenomena. The green-color retention ability of CP- or CCP-treated bamboo was the same as that of CCA-treated bamboo during 12 weeks of weather exposure. Because the CCA- and CCP-treated bamboo could not maintain its vivid green color after 32 days of the light-fastness test, it must be concluded that moso bamboo culms treated with CP have better green-color fastness when exposed to both conditions than those with other treatments.

Conclusions

Various chromium-based reagents were used to treat moso bamboo culms to investigate the effects on the protection and fastness of their green color. Results demonstrated that moso bamboo culms treated with chromated phosphate (CP) exhibited a greener color than those treated with chromated copper arsenate (CCA) or chromated copper phosphate (CCP). The concentration, treatment time, and CrO_3/H_3PO_4 ratio in the CP solution greatly affected the green color of moso bamboo culms. Our results showed that the green color of treated moso bamboo is closest to that of fresh-cut bamboo when samples were treated with 2% CP at 60°C for 3h with a 1:1 CrO_3/H_3PO_4 ratio in aqueous solution. Meanwhile the CP-treated moso bamboo also exhibited excellent color-fastness after exposure to both accelerated UV light fastness and outdoor weathering.

Acknowledgments This work was supported in part by a grant from the National Science Council (NSC-86-2313-B-002-096). We thank the NSC for the financial support and Prof. David N.S. Hon (Clemson University) for his kind suggestions.

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