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Green-color conservation of ma bamboo (*Dendrocalamus latiflorus*) treated with chromium-based reagents

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Abstract The objectives of this study were to search for appropriate chemical reagents without arsenic to use as green-color protectors for ma bamboo (*Dendrocalamus latiflorus* Munro) culms and to compare the effectiveness of these reagents for green-color conservation. Bamboo culms treated with chromated copper phosphate (CCP) or chromated phosphate (CP), which were developed by us, exhibit a greener color than those treated with Boliden K-33 (type B chromated copper arsenate).The experimental results revealed that among the chemicals employed, CrO_3 and H_3PO_4 were key components in conserving the green color of bamboo epidermis, and their ratio definitely affected the effectiveness of green-color conservation. When the CrO_3/H_3PO_4 ratio was 1:1, the treated bamboo culms displayed the greenest color. Among all the bamboo culms treated with different formulations of inorganic salts, the one treated with CP (1% CrO_3, 1% H_3PO_4) had the best green-color conservation, enhanced by increasing the duration of treatment.

Key words Ma bamboo · Green-color conservation · Chromated copper phosphate (CCP) · Chromated phosphate (CP)

Introduction

Bamboo, a perennial lignified plant that belongs to Bambusoideae, is one of the most important forest resources and grows more rapidly than any other woody plant on earth. Most species reach their maximum height of 15–30m in 2–4 months and full maturity in about 3–8 years. Although bamboo thrives naturally on all continents except Europe,[1] most is found in Asia. It is becoming one of the fastest growing renewable natural resources.

Ma bamboo (*Dendrocalamus latiflorus* Munro) is one of the most popular and valuable bamboo species in Taiwan. It fascinates people because of its green color, which is due to abundant chlorophyll on its epidermis, making it different from other woody materials. However, after being harvested, in addition to easy deterioration by insects, pests, and decay, the chlorophylls of bamboo culms are degraded readily owing to the influence of environmental factors, leading to the disappearance of its attractive green color. To overcome this problem and to encourage the bamboo industry to explore the potential utilization and increased economic value of bamboo products using green culms, several inorganic salts, particularly Boliden K-33 [type B chromated copper arsenate (CCA): 35.3% CrO_3, 19.6% CuO, 45.1% As_2O_5] have been examined and proven not only to protect the green surface but also the good performance of green color-fastness.[2,3] At the same time, treatment with CCA-type protectors increased the durability against weathering.[3]

Bamboo culms treated with Boliden K-33 had the best green-color conservation and fastness against weathering,[2,3] but the toxicity of arsenic, a major component in CCA (e.g., Boliden K-33, Tanalith-C) and similar formulations, is a disadvantage. It is known that arsenic preservatives such as CCA are not good for human health and damage the environment as well. Therefore, they are banned in the building industry in some countries such as Finland. To avoid arsenic toxicity, this study sought appropriate chemical reagents without arsenic for conserving the green color of ma bamboo culms and compared the effectiveness of these reagents.

Materials and methods

Materials

Three-year-old ma bamboo was obtained at the experimental forest of National Taiwan University. The fresh bamboo was cut into 4.0 × 1.5 × 0.4cm pieces to be used as speci-

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Table 1. Composition of chemicals used

Chemicals[a]	Composition (%)	Conc. (%)
CCA (chromated copper arsenate)[b]	CrO_3:CuO:As_2O_5 = 35.3:19.6:45.1	5
CCB (chromated copper borate)	CrO_3:CuO:H_3BO_3 = 42.1:17.2:40.7	5
$CuSO_4$	$CuSO_4$	2, 5
Copper naphthenate	Contains 10% copper	5
CCN (chromated copper nitrate)	CrO_3:$CuSO_4$:HNO_3 = 33.3:33.3:33.3	3
CCP (chromated copper phosphate)	CrO_3:$CuSO_4$:H_3PO_4 = 33.3:33.3:33.3	3
CP (chromated phosphate)	CrO_3:H_3PO_4 = 50.0:50.0	2
CC (chromated copper salt)	CrO_3:$CuSO_4$ = 50.0:50.0	2
CuP (chromated copper salt)	$CuSO_4$:H_3PO_4 = 50.0:50.0	2
CrO_3	CrO_3	2
H_3PO_4	H_3PO_4	2

[a]Treatment solutions were formulated in water except the copper naphthenate for which xylene/ethanol (1:1 v/v) was used
[b]Boliden K-33 (type B chromated copper arsenate) was used

mens. To protect the green color of bamboo epidermis, various chemicals were used as protectors, as summarized in Table 1. These treatment solutions were formulated in water, except copper naphthenate, for which xylene/ethanol (1:1, v/v) was used.

Pretreatment

Before treatment with chemical reagents, the bamboo specimens were pretreated at 80°C with 4% potassium carbonate and 1% surfactant mixtures for 30 min to remove the wax layer on the outer surfaces. They then were washed with water.

Chemical treatment

To evaluate the effect of the chemical reagents listed in Table 1 on green-color conservation of ma bamboo culms, after alkali pretreatment the specimens were treated with the various chemical reagents in a 60°C waterbath for 6h and then dried at 60°C for 12h. To find the most appropriate composition of chromated phosphate (CP) on green-color conservation, seven CrO_3/H_3PO_4(%) ratios were investigated: 2:0, 1.6:0.4, 1.2:0.8, 1:1, 0.8:1.2, 0.4:1.6, and 0:2. To study the effect of different times of exposure to the chemical reagent, alkali-pretreated specimens were treated with CP in a 60°C waterbath for four durations (0.5, 1.0, 3.0, 6.0h) and then dried at 60°C for 12h.

Measurement of surface color

The color change of specimens was measured with a color and color difference meter (Dr. Lange Co.), whose light source is D_{65} with a test-window diameter of 5mm. The tristimulus values X, Y, and Z of all specimens were obtained directly from the colorimeter. The recommended CIE (Commission Internationale d'Eclairage) L^*, a^*, and b^* color parameters were then computed, followed by calculating the brightness difference (ΔL^*), the difference of a^* component (Δa^*), the difference of b^* component (Δb^*), the chroma difference (ΔC^*), the hue difference (ΔH^*), and the color difference (ΔE^*) based on the following formulas.[2,4]

$$\Delta L^* = Lt^* - Ls^*$$
$$\Delta a^* = at^* - as^*$$
$$\Delta b^* = bt^* - bs^*$$
$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$
$$\Delta C^* = Ct^* - Cs^*$$
$$\Delta H^* = [(\Delta E^*)^2 - (\Delta L^*)^2 - (\Delta C^*)^2]^{1/2}$$

where Lt^*, at^*, bt^*, and Ct^* are L^*, a^*, b^*, and C^* of the treated sample, respectively; Ls^*, as^*, bs^*, and Cs^* are L^*, a^*, b^*, and C^* of the control reference, respectively; L^* is the value on the white-black axis; a^* is the value on the red-green axis; b^* is the value on the blue-yellow axis; C^* is chroma, i.e., $C^* = [(a^*)^2 + (b^*)^2]^{1/2}$.

Analysis of variance

According to Ott,[5] Duncan's test is a powerful and popular tool for performing a multiple-range test on means of different treatments. Therefore, we employed the test to evaluate the differences of each combination ratio of the CP and treatment times based on the green color of ma bamboo culms. The measured a^* value was analyzed by Duncan's test with a 5% level of significance.

Wettability of specimen epidermis

The wettability of specimen epidermis was evaluated with a contact-angle meter (Kyowa Kaimenkagaku Co.).

Results and discussion

It is well known that a siliceous wax covers the surface layers of bamboo culm[6,7] and interferes with the adhesion properties of coatings. It is speculated that these siliceous wax layers may also interfere with the effect of chemical treatments on green-color conservation of bamboo culm.

Table 2. Surface color and contact angle of ma bamboo before and after pretreatment

Specimens	CIE LAB			ΔC^*	ΔH^*	ΔE^*	Contact angle (°)
	L^*	a^*	b^*				
Fresh	32.7	−5.3	16.7	–	–	–	77.8
Pretreated	29.4	−3.7	14.9	−2.2	−0.1	4.1	66.0

L^*, color parameter on the white/black axis; a^*, color parameter on the red/green axis; b^*, the color parameter on the blue/yellow axis; ΔC^*, chroma difference; ΔH^*, hue difference; ΔE^*, color difference

Ma bamboo pretreated with potassium carbonate–surfactant mixtures proved to be an efficient and reliable method for removing the siliceous wax layer.

Table 2 shows the effect of alkali pretreatment on the surface properties of ma bamboo. After pretreatment, the contact angle of the bamboo epidermis decreased from its original 77.8° to 66.0°. This means that the wettability of bamboo is increased after pretreating it with an alkali solution, which facilitates penetration of subsequent chemical reagents into its surfaces and benefits surface coating. In addition, the CIE LAB color parameters L^*, a^*, and b^* of alkali-pretreated bamboo were 29.4, −3.7, and 14.9 (Table 2), respectively. Meanwhile a slight chroma difference (ΔC^* −2.2) and a hue difference (ΔH^* −0.1) were observed. Thus there was only a minor color variation after the alkali pretreatment.

In our previous paper,[3] ma bamboo treated with CCA-type preservatives (e.g., Boliden K-33) had the best green-color protection. To understand the effectiveness of copper and chromium salts in CCA on the green-color protection of ma bamboo culms, three reagents containing copper – CCB, copper naphthenate, copper sulfate – were primarily used as protectors and were compared with CCA (Boliden K-33)-treated bamboo. The color variation of ma bamboo treated with these reagents at 60°C for 6h is shown in Table 3. The a^* is the value on the red-green axis. That is, a negative a^* value means it is green, and the smaller the a^* value the deeper is the green color. A positive a^* value means red. For the convenience of this discussion, it is reasonable and easier to evaluate the effectiveness of green-color conservation by comparing the a^* values. Comparison of the a^* values in Table 3 demonstrated that, except CCB, all of the reagents employed provided some green-color conservation for alkali-pretreated bamboo. Nevertheless, among these chemical reagents, ma bamboo treated with CCA (Boliden K-33) had the most effective protection, as the a^* value of ma bamboo culm treated with Boliden K-33 was the smallest (−5.5).

Although CCA (Boliden K-33) treatment produces good green-color conservation, the 45.4% arsenic contained in CCA has been recognized as a serious hazard to the environment. Because arsenic belongs to the group Va elements in the periodic table, it was speculated whether green-color conservation could still be achieved if the arsenic component in CCA was replaced by a nitric or phosphoric compound. Accordingly, less toxic CCN (1% CrO_3, 1% CuO, 1% HNO_3) and CCP (1% CrO_3, 1% CuO, 1% H_3PO_4) were

Table 3. Color variation of ma bamboo after treating it with Boliden K-33, CCB, copper naphthenate, and copper sulfate

Specimen[a]	CIE LAB		
	L^*	a^*	b^*
Untreated control	43.1	−1.5	18.0
5% CCA (Boliden K-33)	50.8	−5.5	30.0
5% CCB	34.0	10.9	13.7
5% Copper naphthenate	44.1	−2.5	20.5
5% Copper sulfate	30.2	−1.9	13.3

[a] Alkali-pretreated bamboo

Table 4. Color variation of ma bamboo after treating it with CCN and CCP

Specimen[a]	CIE LAB		
	L^*	a^*	b^*
Untreated control	43.1	−1.5	18.0
3% CCN	41.2	−0.2	16.9
3% CCP	48.9	−9.2	23.5

[a] Alkali-pretreated bamboo

developed as arsenic-free formulations by substituting HNO_3 or H_3PO_4 for As_2O_5. The CIE LAB color parameters of ma bamboo treated with these salts are shown in Table 4. The a^* values of CCN- and CCP-treated bamboo were −0.2 and −9.2, respectively. Comparison with the a^* values demonstrated that ma bamboo treated with CCN was not effective for green-color conservation, but, the specimen treated with the less toxic CCP exhibited a greener color than that treated with 5% CCA (Boliden K-33). In other words, substituting H_3PO_4 for As_2O_5 in CCA can enhance green-color conservation.

To further understand the influence of H_3PO_4 in CCP on the color of ma bamboo, various contents of H_3PO_4 were investigated. The CCP solutions were formulated using 1% CrO_3, 1% CuO, and H_3PO_4 with concentrations from 0% to 1%. By increasing the concentration of H_3PO_4, the a^* value decreased, whereas the L^* value increased (Fig. 1). When the content of H_3PO_4 exceeded 0.6%, neither the a^* value nor the L^* value changed. The b^* value remained constant under different concentrations of H_3PO_4. The results indi-

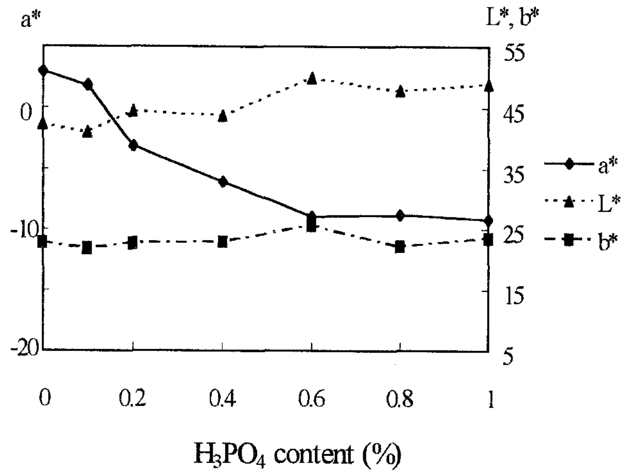

Fig. 1. Influence of H_3PO_4 content in CCP on the color of ma bamboo

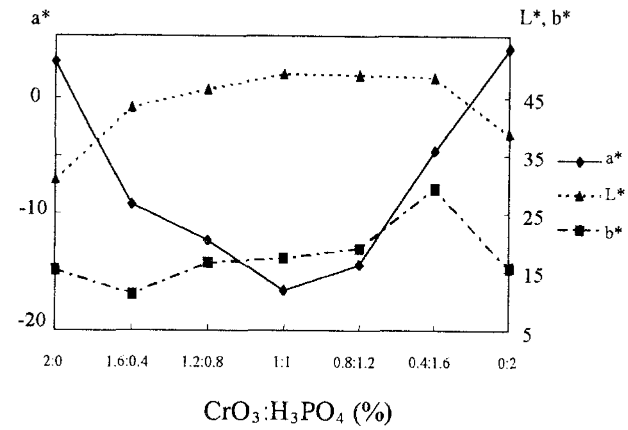

Fig. 2. Influence of CrO_3/H_3PO_4 ratios in CP on the color of ma bamboo

Table 5. Color variation of ma bamboo after treating it with each component of CCP

Specimen[a]	CIE LAB		
	L^*	a^*	b^*
2% CP	48.8	−16.6	17.4
2% CC	44.1	12.0	30.4
2% CuP .	57.4	−5.0	23.7
2% CrO_3	30.0	10.5	10.0
2% $CuSO_4$	30.2	−1.9	13.3
2% H_3PO_4	48.2	5.7	22.7

[a] Alkali-pretreated bamboo

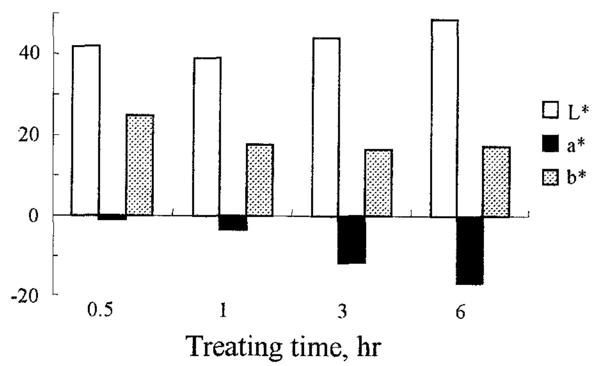

Fig. 3. Color changes of ma bamboo as a function of CP treating time

cated that ma bamboo treated with CCP had a greener color, particularly with 0.6%–1% H_3PO_4.

The influence of each component in CCP was also investigated. The results, shown in Table 5, revealed that ma bamboo treated with CrO_3, $CuSO_4$, or H_3PO_4 separately produced no improvement in green-color conservation; whereas by treating it with a combination of two components, (e.g., CP or CuP) effective protection was obtained. Among all the chemicals used, based on the results in Table 5, the CP-treated specimen has the greenest color. The CIE LAB color parameters L^*, a^*, and b^* were 48.8, −16.6, and 17.4, respectively. Moreover, the brightness of the CP-treated bamboo was similar to that of the CCP-treated one, and the hue tended toward blue ($b^* = 17.4$).

These results demonstrated that both CrO_3 and H_3PO_4 were key components in conserving the green color of bamboo epidermis. Hence, different CrO_3/H_3PO_4 ratios were investigated to find the most appropriate composition of CP. The a^* value, shown in Fig. 2, decreased when we changed the CrO_3/H_3PO_4 ratio from 2:0 to 1:1, whereas it increased when the ratio changed from 1:1 to 0:2. Estimating from the Duncan test, the a^* values were significantly different when the CrO_3/H_3PO_4 ratio changed from 2:0 to 1:1. When the ratio changed from 0.8:1.2 to 0:2, on the other hand, the differences in the a^* values were verified to be statistically significant. No significant variation in the b^* value was observed among the ratios except when the ratio was 0.4:1.6. In addition, the L^* value of bamboo culms treated with CP using a ratio of 1:1 was 48.8, with the brightest color among all CP-treated specimens using the various ratios. It was clear that green-color conservation of bamboo epidermis was best when the CrO_3/H_3PO_4 ratio was 1:1.

When considering practical application for the manufacturing of green bamboo products, it is desirable to reduce the treating time. Therefore, four different times including 0.5, 1, 3, and 6h were examined. The a^* values of bamboo treated with CP (1% CrO_3, 1% H_3PO_4) for 0.5, 1, 3, and 6h, as shown in Fig. 3, were −1.2, −3.4, −11.7, and −16.6, respectively. These differences are statistically significant by Duncan's test. Thus the effectiveness of green-color conservation of ma bamboo culms could be enhanced by increasing the treating time. The ma bamboo treated with CP for 6h had the greenest color; and treatment with CP for 3h could achieve effective green-color conservation similar to that seen after treatment with 3% CCP for 6h.

The evaluation of green color fastness of bamboo treated with chromium-based reagents is ongoing. The results will be published in the near future.

Conclusions

The culms of ma bamboo treated with different reagents have different color changes and green-color conservation. The following conclusions can be drawn.

1. Pretreating ma bamboo culms with potassium carbonate–surfactant mixtures is an efficient, reliable method to remove the cuticles from culm epidermis. After pretreatment, the wettability of bamboo epidermis is improved, and only slight chroma and hue differences were observed.
2. CCP- or CP-treated bamboo culm has a greener color than that treated with CCA (Boliden K-33).
3. The H_3PO_4 content markedly affects green-color conservation in CCP-treated bamboo culm. Green-color conservation is enhanced by increasing the content of H_3PO_4 in CCP, particularly with 0.6%–1.0% H_3PO_4.
4. Among all the chemicals tested, CP produced the greenest bamboo culm, particularly when the CrO_3/H_3PO_4 ratio was 1:1. Moreover, it can be enhanced by increasing the treating time.

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