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Retention of Red Color in Taiwania (*Taiwania cryptomeriodes* Hay.) Heartwood

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Summary

Taiwania (*Taiwania cryptomeriodes* Hay.) is one of economically important tree species indigenous to Taiwan. The heartwood of Taiwania is yellowish red with distinguished purplish pink streaks. Unfortunately, the "red" color is susceptible to change to dull black after exposure the heartwood to natural environment. This discoloration is a serious defect that decreases the value of Taiwania products. In order to preserve the red color of Taiwania heartwood, aliphatic polyurethane (PU) clear coatings containing Tinuvin photostabilizer coupled with pretreatment using photostabilizers, polyethylene glycol (PEG), semicarbazide (SCB) and acetic acid, were used. The experimental results demonstrated that discoloration on the surface of Taiwania heartwood could be prevented by pretreating it with photostabilizers (Tinuvin-1130 and Tinuvin-292) or PEG or SCB, followed by finishing it with a PU coating containing Tinuvin-1130 photostabilizer. The discoloration could be reduced to 30% of that of the untreated specimen by treating it with photostabilizers pretreatment or PEG pretreatment followed by finishing it with a PU coating containing Tinuvin-1130 photostabilizer. Furthermore, the discoloration was proven to reduce to 10% of that of the untreated specimen by treating it with SCB pretreatment followed by finishing it with a PU coating containing Tinuvin-1130 photostabilizer.

Introduction

Taiwania (*Taiwania cryptomeriodes* Hay.) is one of the economically important tree species indigenous to Taiwan. The heartwood of Taiwania is yellowish red with distinguished purplish pink streaks. Unfortunately, the color is susceptible to change to dull black after exposure it to natural environment. This discoloration is a serious drawback that decreases the value of Taiwania products. In a previous study (Wang *et al.* 1994), we have proven that the discoloration of Taiwania panels is caused by the photooxidation in the presence of moisture. The color change in Taiwania heartwood from yellowish red towards bluish green is caused by the combined effects of light and oxygen. Moreover the color is also darkened and eventually turns to black in the presence of moisture. Overall the pronounced discoloration on the surface of Taiwania heartwood is mainly induced by the light with wavelengths in the range of 350–450 nm.

In order to prevent the discoloration of heartwood, we have tried to find appropriate treatments to inhibit such reaction. A great deal of effort has been put into the development of protective systems for wood to prevent photodegradation (Hon and Minemura 1991). Among many methods, coating treatment offers the most simple and effective method for preventing the surface degradation of wood. Although the use of clear coatings to retain the natural texture and color of wood would be very beneficial, the performance of clear coatings against photooxidative degradation is regrettably poor (Chang 1993, 1995; Macleod *et al.* 1995). Most of the available clear finishes are sensitive to ultraviolet light and readily lose their protective functions. Thus, it is necessary to add a photostabilizer into the clear coating or to pretreat the wood surface with a useful chemical to improve the effectiveness of protection. The purpose of this study is to find an appropriate method to retain the red color in Taiwania heartwood.

Material and Methods

Taiwania (*Taiwania cryptomeriodes*) used in this study was collected from the Experimental Forest of National Taiwan University. Taiwania heartwood blocks with dimensions of $3.5 \times 3.5 \times 1.0\,cm^3$ were prepared from a freshly cut log. All specimens were air dried in a dark room with constant temperature and moisture (temp. 20°C; rel. h. 65%). Air-dried red blocks of Taiwania heartwood were finished with aliphatic polyurethane(PU) coatings (Lignal Co.) containing one photostabilizer (Tinuvin-1130) or two photostabilizers (Tinuvin-1130 and Tinuvin-292). Both of photostabilizers were supplied by Ciba Geigy Co.. The amount of each stabilizer used was 1% of the solid content of PU. In order to improve the effectiveness of discoloration prevention, several chemicals including Tinuvin-292, Tinuvin-1130, polyethylene glycol (PEG)(30% PEG, M.W. = 1000), semicarbazide (SCB) (5 g semicarbazide and 7.5 g sodium acetate were dissolved in 50 ml ethanol/water (1/1) solution) and acetic acid (Acid) (pH = 4) were brushed onto the Taiwania heartwood surface before coating. Details of surface treatments are summarized in Table 1.

For an accelerated lightfastness study of surface protected Taiwania heartwood, a Q.U.V. lightfastness tester (Q-Panel Co.) installed with eight UVA-351 fluorescent sunlamps was used. The light exposure was set up for a continuous 24 hours irradiation period. The black panel temperature was 60 ± 2°C during expo-

Table 1. Surface protection treatments of Taiwania heartwood for preventing discoloration

Abbr. of the Chemicals	Pretreatment	Coating
Control	No	No
PU	No	PU
PU (1130)	No	PU + Tinuvin-1130
PU (292)	No	PU + Tinuvin-292
PU (1130 + 292)	No	PU + Tinuvin-1130 + Tinuvin-292
T (1130)	Tinuvin-1130	No
T (1130)/PU (1130)	Tinuvin-1130	PU + Tinuvin-1130
T (292)	Tinuvin-292	No
T (292)/PU (1130)	Tinuvin-292	PU + Tinuvin-1130
T (1130 + 292)	Tinuvin-1130 + Tinuvin-292	No
T (1130 + 292)/ PU (1130)	Tinuvin-1130 + Tinuvin-292	PU + Tinuvin-1130
T (PEG)/PU (1130)	Polyethylene glycol	PU + Tinuvin-1130
T (SCB)/PU (1130)	Semicarbazide	PU + Tinuvin-1130
T (Acid)/PU (1130)	Acetic acid	PU + Tinuvin-1130

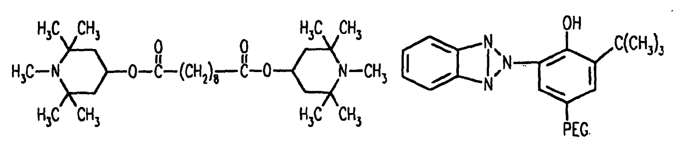
sure. The color measurements of all specimens were conducted using a UV-VIS spectrophotometer equipped with an integrating sphere (Jasco Co.). The tristimulus values X, Y, and Z of all specimens were recorded directly from the spectrophotometer. Then, the recommended CIE (Commission International de l'Eclarirage) L* (lightness), a* (along the X axis red to green), and b* (along Y axis yellow to blue) color parameters and C* (hue) were computed to calculate the color difference(ΔE^*) and hue difference (ΔC^*) based on the following formula: $\Delta L^* = L_t^* - L_0^*$, $\Delta a^* = \Delta a_t^* - a_0^*$, $\Delta b^* = b_t^* - b_0^*$, $\Delta C^* = (a^{*2} + b^{*2})^{1/2}$, $\Delta C^* = C_t^* - C_0^*$, $\Delta E^* = \Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$. Where, subscripts $_0$ and $_t$ are the values obtained before and after exposure. The IR analysis used in this study was carried out by using a Bio-red model FTS-40 spectrophotometer.

Results and Discussion

PU coatings containing photostabilizers to protect Taiwania heartwood

In this study, we selected two kinds of photostabilizers, namely, Tinuvin-292 (HALS, Hindered amine light stabilizer, a free radical inhibitor) and Tinuvin-1130 (hydroxyl phenyl benzotriazole, a UV-absorber), to add into the PU coatings to reduce ultraviolet light penetration into wood surface. The chemical structures of Tinuvin-292 and Tinuvin-1130 are shown in Figure 1. After 96 hours of UV exposure, the color difference (ΔE^*) of various Taiwania heartwood specimens is shown in Figure 2. The surface of uncoated panels(control) showed the most significant color change ($\Delta E^* = 19.8$). Comparison of the color differences of specimens coated with PU without and with photostabilizers, the color variations among PU coating (PU, $\Delta E^* = 9.2$), PU containing Tinuvin-292 (PU(292), $\Delta E^* = 9.1$) and PU containing both Tinuvin-1130 and Tinuvin-292 (PU(1130 + 292), $\Delta E^* = 9.4$) were almost the same. The specimens coated with PU containing Tinuvin-1130 had the least color change ($\Delta E^* = 7.2$). Apparently, the protection effectiveness of PU coating containing Tinuvin-292 and PU coating containing both Tinuvin-1130 and Tinuvin-292 was not better than that of using PU coating alone. These results indicated that the discoloration of Taiwania heartwood panels could be reduced by PU coating containing Tinuvin-1130.

From our previous study (Wang *et al.* 1994), we had scrutinized the effect of wavelength on the discoloration of Taiwania heartwood. We found that the pronounced discoloration on the surface of Taiwania heartwood was mainly induced by the light with wavelengths in the range of 350–450 nm. Thus, if we can minimize the wavelengths 350–450 nm UV light reaching the surface, the discoloration of Taiwania may be reduced. Figure 3 shows the UV absorption spectra of Tinuvin-1130 and Tinuvin-292. Tinuvin-1130 absorbed the light in the wavelengths 260–400 nm. Apparently, Tinuvin-1130 can eliminate the wavelengths that led to the pronounced discoloration on the surface of Taiwania heartwood. Tinuvin-292 absorbed the light with wavelengths 240–260 nm. Unfortunately, these wavelengths do not match the light wavelengths that led to the pronounced discoloration on the surface of Taiwania heartwood. This finding supported the view that PU coating containing Tinuvin-1130 could prevent discoloration of Taiwania effectively. Concerning with the main effect of Tinuvin-292, it reacts with free radicals and thus interrupts degradative chain reactions in the coating films. However,



(a) (b)

Fig. 1. Chemical structures of Tinuvin-292(a) and Tinuvin-1130(b).

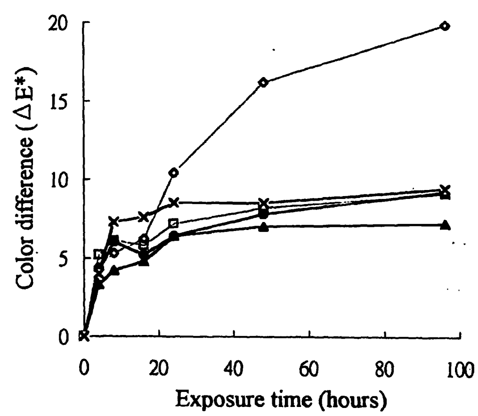


Fig. 2. Changes in color difference of Taiwania heartwood coated with PU containing photostabilizers. Control (◇): untreated sample, PU (●): PU coating, PU (1130) (▲): PU coating containing Tinuvin-1130, PU (292) (□): PU coating containing Tinuvin-292, PU (1130 + 292) (×): PU coating containing Tinuvin-1130 and Tinuvin-292.

the results show that the addition of Tinuvin-292 into PU coating could not inhibit discoloration of Taiwania effectively as PU containing Tinuvin-1130 did. It is known that free radical species are readily generated in wood by light. These radicals rapidly interact with oxygen to produce hydroperoxide impurities that are decomposed easily to produce chromophoric groups. In fact, there are two kinds of discoloration taking place on the coated wood. One is the discoloration of wood and the other is the discoloration of film. The UV absorber (Tinuvin-1130) is not only to prevent the discoloration of film but also to protect the wood surface. Thus, using the Tinuvin-1130 would obtain better preventive result. The use of adding the Tinuvin-292 in PU coating only to quench the free radicals generated from degraded film and could not catch the free radicals from the irradiated wood. In other words, Tinuvin-292 only protected the PU film, thus it had less protective effect than PU(1130). Morever, the addition of both Tinuvin-292 and Tinuvin-1130 into PU coating did not get a better protective effect. It may be due to the incompatibility of these two photostabilizers in the PU coating. Further investigation in this matter is necessary.

Surface pretreatment to protect Taiwania heartwood

Although using PU coating containing Tinuvin-1130 could reduce color change of Taiwania heartwood from ΔE* = 19.8 to ΔE* = 7.2, it could not prevent completely the discoloration of Taiwania heartwood. For further experiments, six reagents, namely Tinuvin-1130 (T(1130)), Tinuvin-292 (T(292)), Tinuvin1130 + 292 (T(1130 + 292)), polyethylene glycol (T(PEG)), semicarbazide (T(SCB)) and acetic acid (T(Acid)) were used to pretreat Taiwania heartwood before coating. The results of color change of pretreated Taiwania heartwood after 96 hours of UV irradiation are shown in Table 2. It is obvious that all of the pretreatments could decrease the color change of Taiwania heartwood. Surface pretreatments using three kinds of photostabilizers without PU coatings such as T(1130), T(292) and T(1130 + 292) can reduce the discoloration of Taiwania heartwood. Actually, the effectiveness of T(1130) (ΔE* = 8.4) and T(1130 + 292) (ΔE* = 7.1) was better than that of the PU coating(PU, ΔE* = 9.2). It indicated that surface pretreatments with photostabilizers could also significantly decrease the color change of Taiwania heartwood. A synergistic effect was observed when Taiwania heartwood was pretreated with both Tinuvin-1130 and Tinuvin-292 (T(1130 + 292), ΔE* = 7.1).

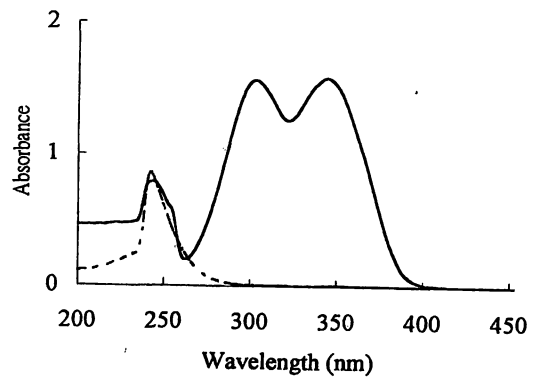


Fig. 3. UV spectra of Tinuvin-1130 (–) and Tinuvin-292 (. . .).

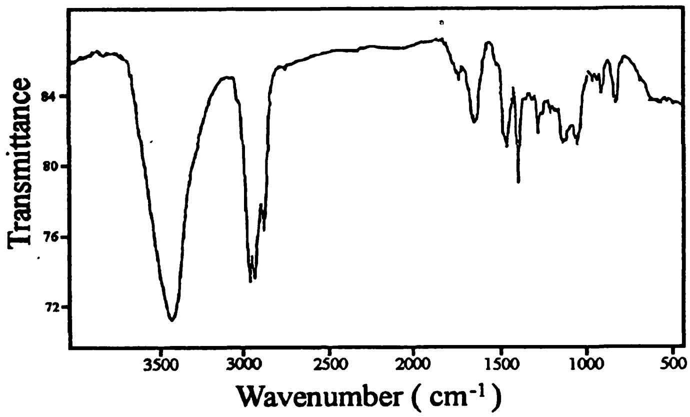


Fig. 4. Infrared spectrum of n-hexane subfraction from Taiwania.

$$\text{Wood} - C = O \quad + \quad H_2NCONHNH_2$$
$$\downarrow$$
$$\text{Wood} - C = NCONHNH_2$$

Fig. 5. Reaction of semicarbazide with carbonyl groups.

It has been reported that α-carbonyl, conjugated carbon-carbon double bond and phenolic hydroxy groups are the principal chromophoric groups in wood, they must be modified to reduce discoloration(Hon and Minemura 1991). In accordance with our previous study (Chang *et al.* 1996), however, the n-hexane soluble and methanol soluble extractives of Taiwania heartwood were the most light-sensitive elements. Figure 4 is the infrared spectrum of n-hexane subfraction from the Taiwania heartwood. It shows that there are carbon-carbon double bond ($1640\,cm^{-1}$) and carbonyl groups($1700\,cm^{-1}$) in the n-hexane subfractionated portion. They are unstable functional groups which contribute to the light-sensitiveness of Taiwania heartwood. In this study we applied semicarbazide to modify the carbonyl groups in the Taiwania heartwood extractives. The scheme of semicarbazide reacting with carbonyl groups is shown in Figure 5. From Table 2 it is obvious that Taiwania heartwood pretreated with semicarbazide (T(SCB)) has a reduced color change (reduced ΔE* from 19.4 to 9.4). The changes of a* (Δa*) of T(SCB) was 1.6 (shifted to red). This suggested that pretreatment of Taiwania heartwood with semicarbazide could retain the red color of Taiwania under UV exposure.

Table 2 showed that Taiwania heartwood pretreated with PEG (T(PEG)) could decrease the color change from ΔE* = 19.8 to ΔE* = 9.5 after 96 hours of light exposure. In contrast to other pretreatments, the ΔL* of T(PEG) was 6.3 (plus value, increase brightness), indicating that Taiwania heartwood had been bleached by UV irradiation. It was very reasonable because PEG, after irradiation with light, will produce hydroperoxide (Fig. 6) that will bleach wood (Minemura and Umehara 1979, 1986, 1991). It was proven to be very useful to prevent Taiwania heartwood from changing to darker color.

In analyzing the red and discolored (black) Taiwania heartwood, it was found that the pH value increased from 5.78 to 6.42 when the color of Taiwania heartwood increased its darkness (Chang *et al.* 1996). Thus, we used acetic acid (T(Acid)) to pretreat Taiwania heartwood. Result is also shown in Table 2. It was clear that the pretreatment of Taiwania with acetic acid was not effective in preserving the red color because the Δa* of T(Acid) (Δa* = –7.8) was equal to the Control (Δa* = –7.8).

Combination of pretreatment with PU coating containing photostabilizer to protect Taiwania heartwood

As discussed, pretreatment of Taiwania heartwood surface with photostabilizers, PEG and SCB could preserve the red color of Taiwania heartwood. The same effectiveness was obtained by coating Taiwania heartwood with PU containing Tinuvin-1130. It is anticipated that the combination of both treatments could enhance the protective effectiveness. The color variation of Taiwania panels pretreated with chemicals and followed by coating with PU containing photostabilizer (Tinuvin-1130) is illustrated in Figure 7. The color change (ΔE*) of untreated Taiwania heartwood was 19.8 when it was irradiated with light for 96 hours. When it was treated with photostabilizers (Tinuvin-1130 and Tinuvin-292) and PU coating (T(1130 + 292)/PU (1130)), the ΔE* reduced to 6.2 under identical irradiation conditions. Likewise, when it was treated with PEG and PU coating containing Tinuvin-1130(T(PEG)/PU(1130)) as well as with semicarbazide and PU coating containing Tinuvin-1130 (T(SCB)/PU(1130)), the ΔE* were 5.0 and 6.4 respectively. It appears that PU coating applied to pretreated wood would increase the effectiveness of color retention. In order to provide better illustration of treatment effectiveness, ΔC* $((\Delta a^{*2} + \Delta b^{*2})^{1/2})$ was calculated and compared. The changes of hue (ΔC*) of surface protection is explicated in Figure 8. The experimental results demonstrated that the discoloration could be reduced to 30 % of that of the untreated specimen by treating it with T (1130 + 292)/PU (1130) and T (PEG)/PU (1130). Furthermore, the discoloration was proven to be reduced to 10 % of that of the untreated specimen by treating it with T (SCB)/PU (1130).

Table 2. Color changes of Taiwania heartwood pretreated with chemical reagents after 96 hours of UV irradiation

Specimens	ΔL*	Δa*	Δb*	ΔE*
Control	–9.7	–7.8	–15.4	19.8
T (1130)	–6.8	–4.2	– 2.5	8.4
T (292)	–6.1	–5.4	– 9.2	12.3
T (1130 + 292)	–5.5	–3.5	– 2.8	7.1
T (SCB)	–7.8	1.6	4.9	9.4
T (PEG)	6.3	–2.1	– 6.8	9.5
T (Acid)	–5.7	–7.8	– 3.2	10.2

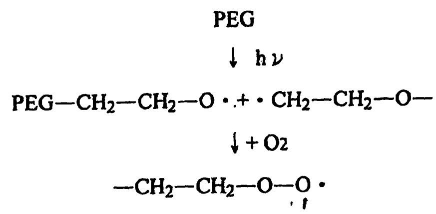


Fig. 6. Free radicals generated from the cleavage of PEG after irradiation with light.

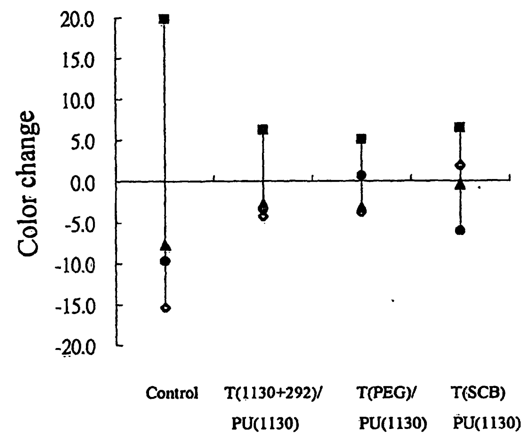


Fig. 7. Color change of surface-protected Taiwania heartwood after 96 hours of UV irradiation. (●: ΔL*, ▲: Δa*, ◇: Δb*, ◘: ΔE*).

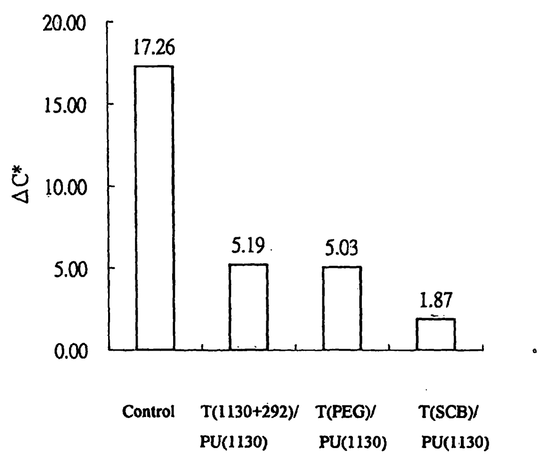


Fig. 8. Change of hue of surface-protected Taiwania heartwood after 96 hours of UV irradiation.

Conclusions

Color is one of the most distinctive properties of wood, and is of considerable esthetic value in woods that are used for decorative purposes. For increasing the commercial value of Taiwania heartwood, it is necessary to retain its red color. In order to preserve the red color of Taiwania heartwood, aliphatic PU clear coatings containing Tinuvin-1130 photostabilizer coupling with pretreatments using photostabilisers, semicarbazide (SCB), polyethylene glycol (PEG), acetic acid were used. The experimental results demonstrate that discoloration on the surface of Taiwania heartwood could be prevented by pretreating it with photostabilizers, namely Tinuvin-1130 and Tinuvin-292 (T (1130 + 292)), PEG (T (PEG)) or SCB (T (SCB)), followed by finishing it with PU coatings containing Tinuvin-1130. The discoloration could be reduced to 30 % of that of the untreated specimen by treating the Taiwania heartwood with T (1130 + 292)/PU (1130) and T (PEG)/PU (1130). Furthermore the discoloration was proven to be reduced to 10 % of that of the untreated specimen by treating it with T (SCB)/PU (1130). Since these methods we used to retain the red color of Taiwania are two-steps surface treatments, it is believed that they are feasible to apply to Taiwania wood products with different dimensions in the production process.

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