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NOTE

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Weathering durability of CCB-impregnated wood for clear varnish coatings

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Abstract Outdoor performances of a polyurethane varnish and an alkyd-based synthetic varnish coated over chromium-copper-boron (CCB)-impregnated Scots pine (*Pinus sylvestris* L.) and chestnut (*Castanea sativa* Mill.) [10 (R) × 100 (T) × 150 (L) mm] were investigated. These varnishes were also applied to the wood surface as sole coatings or impregnated into wood as water-repellent (WR) solutions. Outdoor exposure was performed in the Black Sea region of northern Turkey (41°N, 39.43°E) where humid weather predominates throughout the year and accelerates decomposition of coated wood surfaces. The wood panels were exposed at 45° south on their tangential surfaces. After 9 months of exposure to summer, autumn, and the following winter season, the color and glossiness changes of the exposed surface, adhesion of the coating layer to the wood surface, water absorption through the coating layers, mass loss, and the hardness of the board surface were studied. CCB impregnation greatly stabilized the surface color of varnish-coated panels of both wood species. Gradual decreases of adhesion between varnished layers and preimpregnated surfaces were attributed to probable weakening of interactions at the interface of the treated wood and the film layer. A superficial cleaning process of treated wood is suggested to improve glossiness and adhesion. The coated wood surface became harder with time on outdoor exposure until a maximum hardness occurred followed by softening, whereas the uncoated surface softened steadily. Polyurethane varnish yielded a harder surface than synthetic varnish. Mass losses of wood panels after 9 months of exposure were negligible for all treatments compared with the untreated controls, which were totally discolored and eroded on the surface. It is concluded that long-term exterior wood protection has been achieved by a successful combination of an appropriate preservative treatment followed by a compatible surface-coating process.

Key words Weathering · CCB · Varnish coating · Exterior wood · Chromium · Boron

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Introduction

Outdoor conditions can cause rapid degradation of wood surface primarily due to the effects of ultraviolet (UV) light and water. Paints and varnishes are used to protect the wood surface from weathering as well as for decorative purposes. Design of unpainted wood in exterior construction has created a demand for clear finishes that preserve the natural beauty of wood.[1] However, transparent film-forming finishes, such as spar, urethane, and marine varnishes, are not generally recommended for exterior use on wood because they allow transmission of sunlight, and surface degradation can take place underneath the coatings.[2–4] As a result, coating alone imparts to wood only superficial protection against some deteriorating agents for a limited time, often less than 2 years.[3] The primary aim, then, is not to find or make a varnish capable of withstanding exterior exposure but, rather, to prevent UV-light degradation of the wood itself.[5] Therefore, impregnation of wood with an appropriate water repellent or applying a varnish-compatible preservative chemical prior to coating for exterior use under hazardous service conditions has been undertaken to make wood more stable primarily against photochemical degradation, dimensional changes, biological decomposition, and fire.[3,6] Coating impregnated wood enables safe handling in addition to imparting an aesthetic appearance.

Accordingly, in a natural weathering trial pretreatment of wood with chromium trioxide or chromium nitrate retarded the deterioration of Western red cedar (*Thuja* *pilicata* D. Don) and Douglas fir (*Pseudotsuga menziesii* Mirb. Franco) after 30 months' exposure.[7] Chromated copper arsenate (CCA) impregnation proved to be more effective in extending lifetime and durability of a partially UV light-transparent (semitransparent) stain than brush-applied chromium oxide.[8] The chromium oxides in CCA, which bond to the wood after treatment, decrease photodegradation of the wood surface and can increase two- to threefold the durability of semitransparent stains.[3] It has been shown that the reaction between chromium and phenolic lignin is responsible for photostabilization of the lignin by chromium compounds.[9–11] It has further been postulated that sodium borohydride reacted with the chromium trioxide–guaiacol complex to yield a leach- and weather-resistant acetate polymer,[12] which suggested a potential use of borates in exterior wood preservation. Relatively few studies have been done on the weathering resistance of wood treated with borates or boron/chromium-containing preservatives. Sell et al.[13] tested outdoor weathering durability of surface-treated Obeche, red beech, spruce, and fir wood with chromium-copper-boron (CCB). High resistance of the CCB-coated wood against weathering has been attributed to the protective effect of Cr-Cusalt solutions on the wood surface. The erosion properties of CCB-treated wood surface were supportive of their findings.[14]

Accordingly, CCB was considered for pretreatment as a chromium/boron-containing preservative. The bioactive and relatively high environmental safety of CCB-containing boron instead of arsenic-containing formulations has also attracted attention. Although it is believed that boron-treated wood can withstand outdoor exposure in the case of water-shedding coatings,[15] the extent of the protective effect of different coating systems may vary. Peylo and Willeitner[16] suggested that water-repellent (WR) coatings on borate-treated wood increase the wood's service life. Therefore, chromium in CCB was expected to protect the wood surface against UV-light degradation as copper and boron enhances the biological resistance of wood coincidentally. Surface coating was considered to support a longer-lasting life of CCB-impregnated wood. Based on these premises, the outdoor performance of two commercial varnish types (a polyurethane varnish and an alkyd-based synthetic varnish) applied as coating or WR impregnants of wood were studied in relation to CCB pretreatment. Surface qualities of panels after 9 months of outdoor exposure were then evaluated.

Experimental

Chemicals, impregnation process, coating systems

Wood panels 10 (radial) × 100 (tangential) × 150 (longitudinal) mm were prepared from air-dried sapwood of Scots pine (*Pinus sylvestris* L.) and chestnut (*Castanea sativa* Mill.). The oven-dried specific gravities of these species were measured as 0.49 and 0.58, respectively. Annual growth rings were arranged to make an angle of 45° to the radial edge at cross sections. CCB aqueous solution of 7.5% concentration was prepared from the dry salt supplied by Korusan (Istanbul), composed of 25% boric acid, 36% sodium bichromate, 37% copper sulfate, and 2% additives. An alkyd-based synthetic varnish (Polimarin boat varnish) and a polyurethane varnish of a two-component type consisting of an aliphatic isocyanate-terminated component and an active hydrogen-bearing monomer, which when blended cures at room temperature with 4–5 h pot life of the blend (Ekodur Poliuretan bright varnish, Polisan Chemical Co. of Turkey)[17] were applied separately over untreated and CCB-impregnated wood (Table 1). They were also impregnated into the wood as WR solutions prepared by dissolving the varnishes in white spirit (20% v/v) containing 1% paraffin wax, which reportedly has no effect on proper adhesion of the paint if it is allowed to cure sufficiently after treatment.[3] Specimens were vacuumed for 30 min before introducing the CCB or WR treatment solutions. Then they were allowed to absorb a solution at atmospheric pressure for 30 min. After impregnation, wood panels were conditioned for 3 weeks at 65% relative humidity (RH) and 20° ± 1°C before coating. Weight gain of the specimens due to chemical loading was calculated as follows.

$$\text{Weight gain } (\%) = \frac{W_f - W_i}{W_i} \times 100 \tag{1}$$

where W_f is the final conditioned weight of a wood block and W_i is the initial weight.

Table 1. Treatment systems applied to wood panels prior to outdoor exposure

Treatment group	Impregnating concentration	Varnish type
Untreated (control)	–	–
Untreated (coating alone)	–	Polyurethane
Untreated (coating alone)	–	Synthetic
CCB[a]	7.5% Aqueous solution	Polyurethane
CCB	7.5% Aqueous solution	Synthetic
WR[b] impregnation with polyurethane varnish	20% Dissolved in white spirit includes 1% paraffin wax	Polyurethane
WR impregnation with synthetic varnish	20% Dissolved in white spirit includes 1% paraffin wax	Synthetic

[a] Chromium-copper-boron
[b] Water repellent

Filler was not used to avoid any of its potential interference in glossiness and adhesion of coating. Instead, for untreated and CCB-impregnated panels varnish was applied twice as primer coating for filling the voids and as a topcoat to reveal the absolute effect of weathering through the clear varnish layers. The WR solution was considered to function as a primer coat in a WR–impregnation–varnish coating treatment system. Sufficient time for layer settling (20–25 min) was allowed between successive applications until reaching the target retention of 75 g/m^2 for primer and 100 g/m^2 for topcoat controlled by consecutive weighing. Specimens were left at ambient conditions for 24 h before the top coating was applied according to the instructions given by the manufacturer for the varnishes. Surfaces were gently sanded with No. 220 abrasive paper to obtain a smooth surface prior to applying the topcoat.

Each treatment group consisted of 12 individual panels. In total, seven groups of wood panels for each species were exposed to outdoor conditions (Table 1). Differences of surface qualities after exposure between the varnish-coated CCB-impregnated wood and the same varnish-alone-coated wood are considered to reflect the effect of CCB on weathering durability.

Outdoor exposure

ASTM D 358-55[18] was considered during panel preparation for outdoor exposure. All noncoated edges and back sides of the panels were sealed with a polyamide-cured epoxy resin prior to exposure at 45° south on their tangential surfaces on wooden decks installed 50 cm above the ground. Direct contact between the specimens and the wooden frame was avoided by wrapping the frame smoothly with aluminum foil. Because the outdoor weathering process is closely related to the climatic conditions of the place where wood is exposed,[19] a test site was established close to the Regional Meteorological Observation Station in the Black Sea Region at Trabzon (a coastal city in Turkey located at 41.00°N, 39.43°E) to enable practical assessments. Climatic data of the test site during the exposure periods from June 1996 until March 1997 were recorded.

Changes in surface color and glossiness

The color of the specimen was measured by a colorimeter (Minolta, type CR 231; light type D65; filter type silicon photocell). The measuring spot was adjusted to be equal or not more than one-third of the distance from the center of this area to the receptor field stop. The color difference, (ΔE^*) was computed for each panel as follows.[20]

$$\Delta E^* = \sqrt{\left(L_n^* - L_o^*\right)^2 + \left(a_n^* - a_o^*\right)^2 + \left(b_n^* - b_o^*\right)^2} \qquad (2)$$

where L_n^*, a_n^*, and b_n^* are the average color measurements at time n; and L_o^*, a_o^*, and b_o^* are the average color measurements at time o, made at three different points of six panels from each treatment group.[21]

The luminous fractional reflectance of the specimens, which is the average of L^* at those times, was measured according to ASTM D 523-67[22] by a measuring device (Erichsen GmbH, model 507M) consisting of an incandescent light source furnishing an incident beam, a means for locating the surface of the specimen, and a receptor located to receive the required pyramid of rays reflected by the specimen. The receptor is a photosensitive device responding to visible radiation. Results are reported as specular gloss readings. The chosen geometry was an incidence angle of 60.0° ± 0.1° for comparing the specular gloss of the coated panels with the receptor aperture of 4.4° ± 0.1° in the plane of measurement. 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. Six panels from each group were measured at three points for each specimen.

Adhesion of coating film to the wood surface

The ASTM D 3359-95[23] test method B cross-cut tape test was undertaken to assess the adhesion of coatings to the wood. After curing the coating by air-drying, panels were held firmly in a jig, and then six cross-cuts, 1 mm apart, were made manually on the coated surface using a scalpel and a steel ruler. The detached flakes or ribbons of coating were removed from the surface with a soft brush. A strip of fiber-reinforced cellulose acetate pressure-sensitive tape, 20 mm wide and 60 mm long, was then placed over the surface of the blocks. The tape was manually smoothed, and pressure was applied using a rubber eraser to ensure good contact between the tape and the coating film. After 90 ± 30 s of application, the tape was removed from the coated surface by rapidly pulling it off, back upon itself, at an angle as close to 180° as possible. The grid area was inspected for removal of coating from the panel surface using an illuminated magnifier. The rate of adhesion was averaged for six panels of each group based on the code given in the standard for classification.

Water absorption through film layer

A water droplet test was applied to determine the water-repellent efficacy of coating systems before and after outdoor exposure. The diameter of diffused water from five individual droplets (0.047 ± 0.003 g/drop) on a single panel at different locations were measured 3 min after the water dropped. Three randomly selected panels representing 12 panels in each group were tested.

Mass loss

The mass loss of the test panels during weathering was calculated based on the initial (W_i) and the final (W_f) conditioned weight.

Table 2. Monthly averages of climatic measurements of the test site during outdoor exposure of wood panels

Season	Temperature[a] (°C)	RH[a] (%)	Rainfall[a] (kg/m^2)	Wind (m/s)	Cloudiness (total days/month)
Summer 1996					
June	19.3 ± 2.4	76.4 ± 2.7	2.1 ± 0.9	0.69	22
July	24.1 ± 1.8	78.7 ± 5.0	0.7 ± 0.6	0.67	21
August	23.4 ± 0.9	80.2 ± 2.6	3.1 ± 2.7	0.67	20
Autumn 1996					
September	22.8 ± 0.7	77.6 ± 3.0	11.8 ± 3.6	0.89	20
October	16.9 ± 1.8	80.8 ± 2.5	8.4 ± 3.9	0.83	12
November	13.0 ± 1.7	71.8 ± 4.2	5.6 ± 4.5	0.64	16
Winter 1996–1997					
December	12.5 ± 1.5	71.5 ± 10.1	4.4 ± 1.9	0.81	18
January 1997	7.4 ± 3.5	77.8 ± 2.5	7.9 ± 6.8	0.86	16
February 1997	5.6 ± 2.9	69.3 ± 10.4	4.7 ± 2.4	0.72	11

[a] Results are means ± SD

$$\text{Mass loss}\,(\%) = \frac{W_i - W_f}{W_i} \times 100 \quad (3)$$

Each of the 12 panels in all of the groups were weighed.

Surface hardness

The König pendulum damping test was performed to detect the König hardness of the coating according to ASTM D 4366-95.[24] The device (Erichsen GmbH, model 299/300) was calibrated in due course. Test panels were placed on the panel table, and a pendulum was gently placed on the panel surface. The pendulum then was deflected through 6° and released while simultaneously starting a stopwatch. The time (seconds) for the amplitude to decrease from 6° to 3° was determined to be the König hardness. Six replications were conducted for each treatment group.

Results and discussion

The FT-IR analysis of the exposed surfaces has been reported in another paper.[17] Climatic data during the seasons of exposure are given in Table 2. Normal levels of daily temperature (19°–23°C) and remarkably high RH (70%–80%) due to rainfall with a moderate level of sunlight during the summer and autumn seasons at the test site were considered a humid and mild weathering environment. However, cold weather became dominant throughout the winter, with an average daily temperature of 8.5°C, and was considered to well reflect the relative weathering resistance of coated panels at severe climatic conditions.

Color stability

Color differences (ΔE) are given in Table 3 along with the weight gain of the panels due to the impregnated chemicals. Impregnants were retained in larger amounts by Scots pine wood because of the easy penetrability of this species compared to chestnut.[6,25] Although chestnut wood was loaded with a smaller amount of the chemicals due to superficial penetration, the retained amount in wood was considered enough to reflect the impregnants' relative effects on the tested weathering properties.

The results indicated that the color of the untreated, noncoated panels of both species drastically changed after being exposed to outdoor conditions, and the change accelerated during winter, after 7–9 months of exposure (Table 3). Among the tested treatment systems, CCB impregnation of the panels prior to coating with either varnish resulted in the best color stabilization of the surfaces of both species. Surface coating alone with polyurethane varnish resulted in marked color changes after 6 months of exposure during the summer and autumn seasons for both wood species owing to the effect of relatively higher daily temperature caused by effective sunlight[26] during these seasons. Six percent of the total available sunlight energy is primarily responsible for surface discoloration accompanied by the effects of the other major factors in the deterioration of organic polymers, such as oxygen and moisture, particularly with outdoor exposure.[27] The high ΔE of polyurethane-alone-coated surfaces cannot be easily attributed to the potential discoloration of polyurethane varnishes upon exposure to weathering because the presently used type contained an aliphatic isocyanate known to give the varnish better resistance to discoloration, hydrolysis, and heat degradation than aromatic types, which undergo discoloration to yellow on prolonged exposure to sunlight, presumably because of oxidation of some terminal aromatic amine.[27] The high gloss retention of clear urethane coatings and its well known ability to withstand weathering[27] might cause the wood surface to be exposed to sunlight that resulted in photodegradation of the untreated wood surface, which may account for the measured color difference. This evaluation was supported by the ΔE values of WR-impregnated panels with polyurethane (Table 3), consistent with the suggestion of Cassens et al.[28] that wood be treated with a paintable WR preservative first to improve its coating performance. In this case, paraffin wax might disperse or absorb the sunlight on the wood surface even when added at a

Table 3. Color changes (ΔE) of wood panels due to outdoor exposure

Treatment chemical	Weight gain (% w/w)	Varnish type	ΔE	
			After 6 months	After 9 months
Scots pine				
Untreated	–	–	14.0	40.2
Untreated	–	Polyurethane	20.7	20.8
Untreated	–	Synthetic	4.9	7.0
CCB[a]	27.1	Polyurethane	4.1	1.8
CCB	27.1	Synthetic	3.1	1.6
Polyurethane-WR[b]	20.8	Polyurethane	8.6	12.3
Synthetic-WR	33.5	Synthetic	7.1	12.2
Chestnut				
Untreated	–	–	11.0	28.3
Untreated	–	Polyurethane	28.1	27.9
Untreated	–	Synthetic	6.1	8.2
CCB	3.3	Polyurethane	2.2	2.5
CCB	3.3	Synthetic	7.0	5.7
Polyurethane-WR	6.2	Polyurethane	6.0	8.1
Synthetic-WR	3.8	Synthetic	9.0	9.9

[a] Chromium-copper-boron
[b] Water repellent

limited concentration in the varnish solution (1%). If impregnated, varnish acts as a multilayer coating that may further reduce sunlight diffusion into wood. Synthetic varnish generally produced better color stability of the panels of both species, whether coated alone or over WR treatment, consistent with earlier assessments on alkyd-based coatings.[29] However, pretreating wood with a UV stabilizer compatible with polyurethane or adding it to the varnish solution was found necessary. Feist[30] reported that, given good construction practice, any pretreatment (WR, a WR preservative, or similar material) would help protect painted wood from decay and improve the overall performance of both wood and the finish. The tendency of ΔE of the WR-impregnated Scots pine to increase with the continued weathering period (Table 3) indicated that this generalization must be addressed regarding the relative performances of WR types on individual wood species with reference to the season and the specific weathering properties during exposure. CCB, in this aspect, has been compatible with either type of clear varnish in terms of color stabilization of the coated wood surface.

Glossiness

Data for the specular gloss of the coated surfaces of the test panels at a 60° incidence angle measured before and after exposure to weathering are given in Figs. 1 and 2 for both wood species. The film layers of both varnishes were highly glossy before weathering and reflected well the natural appearance of the wood surfaces. CCB impregnation limited glossiness to a point in Scots pine before exposure owing possibly to the absorption and dispersion of the reflected rays by salt crystals prominent in the large lumens of the tracheids of the wide earlywood sections of the grains. $Cr_2O_7^{2-}$ ions are present in the CCB solution because the chromate compound in CCB is the same one used in CCA; and as with CCA, $HCrO_4^-$ dominates in contact with wood.[31,32] The $HCrO_4^-$ ion is usually cited as photoactivate or of the same species, but sometimes the CrO_7^{-2} ion is implicated as well. Thus, the presence of this photoactive ion on the wood surface was assumed to cause some loss in glossiness of the varnishes coated on Scots pine panels before exposure even it contributed to color stability upon exposure (Table 3) and became less effective in terms of glossiness as weathering progressed (Fig. 1). By contrast, the glossiness of unexposed chestnut panels was almost independent of CCB impregnation due largely to the reduced effect of salt crystals during light absorption in the denser wood structure. This suggests that proper impregnation of wood, which has naturally bright surfaces, and cleaning excess chemical from the surface prior to coating are necessary to improve glossiness, as also is required for producing a good coating base.[26] Feist and Williams[8] reported that the durability of the semitransparent stain on CCA-impregnated wood was much better than that of the stain on the wood brush-treated with chromium trioxide solution. Thus, chromium's effect on decreasing the rate of surface degradation caused by UV light is useful when it is deposited in the wood cell wall rather than accumulated on the surface because the chromium ion that precipitates on the treated wood surface can react to strengthen the pigmentation.[31] Photoactivation is a possible contributing factor of chromium ions on the surface. Direct sunlight warms the exposed parts of the surface and increases the rate of chromium reduction to Cr^{3+} twofold for each 7°C increment. Although the presence of chromium in sufficient concentration on the wood surface greatly decreases the rate of wood erosion caused by UV light-induced degradation,[30] chromium was much more effective against erosion when fixed in the cell wall than when on the wood surface.[7] Furthermore, the amount of chromium on the treated wood surface

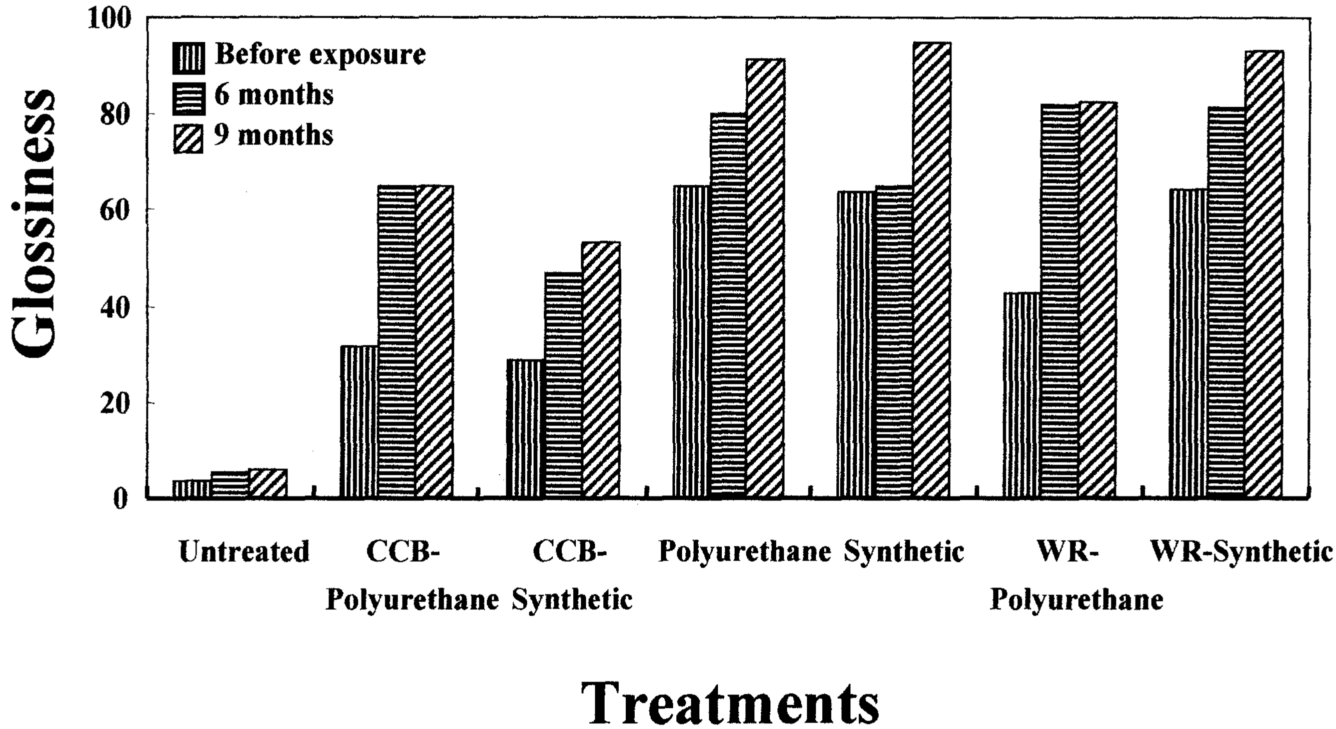

Fig. 1. Specular gloss of varnishes coated over Scots pine surface exposed to weathering

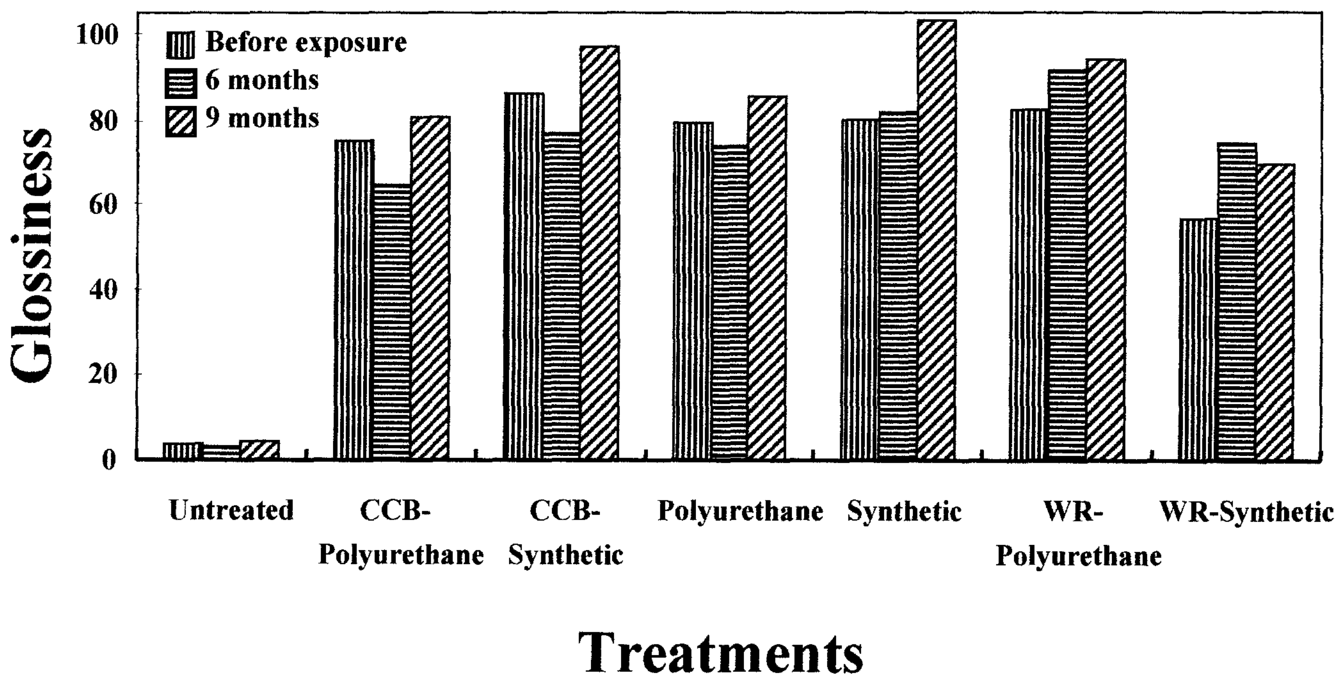

Fig. 2. Specular gloss of varnishes coated over chestnut surface exposed to weathering

must be reduced to eliminate color variations for aesthetic demands. Pizzi and Kubel [33] showed that CCB presents a higher final Cr^{6+} content and lower Cr^{3+} content than CCAs of type C, which indicates that less chromium leaches from CCB-treated wood than from CCA-C-treated wood during the same period of time and under identical conditions. The larger amount of Cr^{6+} forming insoluble precipitates also tends to indicate better waterproofing by CCB than by CCA. Therefore, the color stability effect of CCB can reasonably be expected for longer exposure periods, as it im-

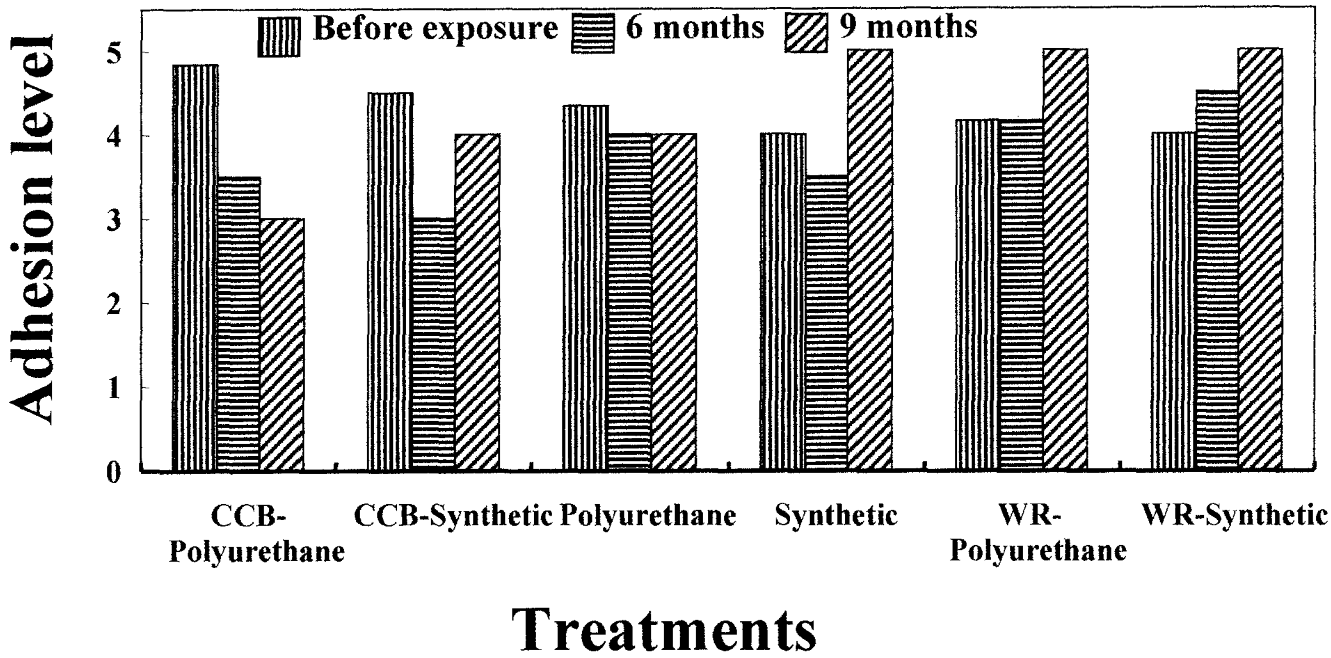

Fig. 3. Adhesion of varnish film to the Scots pine surface exposed to weathering

parts to the varnish-coated wood surface an important color stability even at earlier periods of weathering, though it caused initial glossiness losses of the varnishes applied over bright surfaces of Scots pine (Table 3, Fig. 1).

A significant increase in glossiness was generally recorded for synthetic varnish-alone-coated panels of both wood species (Figs. 1, 2) and was attributed to the relatively high sensitivity of this varnish type to outdoor weathering that positively affected glossiness over time. The ability of a coating to retain its desired gloss during service is of great significance for maintaining an aesthetic appearance of the coated surface for longer periods.[34] It is a common phenomenon that the glossiness of coated surfaces by varnish increases with outdoor or artificial exposure. Because the surfaces are generally rough (microscopically) after coating with brushing or spraying, abrasion (along with weathering erosion) of the surface causes gloss degradation. The erosion effect alone, however, has not been the cause of gloss change of the varnish-coated surface of CCB-treated wood after 9 months' exposure. The present data showed that glossiness of both varnish types changed with the seasons, due mainly to the climatic conditions.[26] Although none of the applications showed drastic gloss degradation, further data of the continuing weathering periods will clearly indicate the development of glossiness.

Adhesion of coating systems

Adhesion of the coatings appeared satisfactory at first for CCB-impregnated wood and was not significantly affected after exposure for 9 months (Figs. 3, 4). However, a gradual decrease suggests that there might be weakening of the interactions at the interface between treated wood and the film layer outdoors during the next exposure periods, though a similar trend in adhesion loss has also been observed for the panels only coated and those coated after WR impregnation. Synthetic varnish tended to regain or kept some of its adhesion during the winter season after a loss during the first two seasons of exposure, somewhat similar to the improved adhesion of alkyd emulsion paint on wood pretreated with Cu-containing preservatives, such as CCA and bis-(*N*-cyclohexyl-diazenium dioxide)-copper (Cu-HDO), reported by Bardage and Bjurman.[35] On the other hand, adhesion of a varnish layer is closely related to its wetting and setting mechanisms of a specific substance[36] so it is likely that, in addition to the differences in anatomical structure of the wood species and being exposed to climatic conditions, it is affected by pretreatment.

Film-forming coatings generally do not penetrate cell walls and thus do not raise the grain of wood.[36] It seems plausible that the force of adhesion of such coatings to wood is due to surface adsorption to the cellulose fibers. Thus stronger hydrogen bonding between the cellulose and water from consecutive wetting by rain displaces the adhered coating from the surface. The presence of a hygroscopic salt on or near the wood surface might have accelerated this process.[37] However, the absence of adhesion loss of the coating layers to the CCB-impregnated wood surface before exposure indicated that it is unlikely that hygroscopicity is the reason for loosened adhesion. On the contrary, leach- and weather-resistant acetate formation might have been expected on the wood surface based on the postulated reactions between boron and the chromium–phenolic lignin complex.[12] Therefore, a superficial surface cleaning process prior to coating seems to improve adhesion for longer exposure periods.

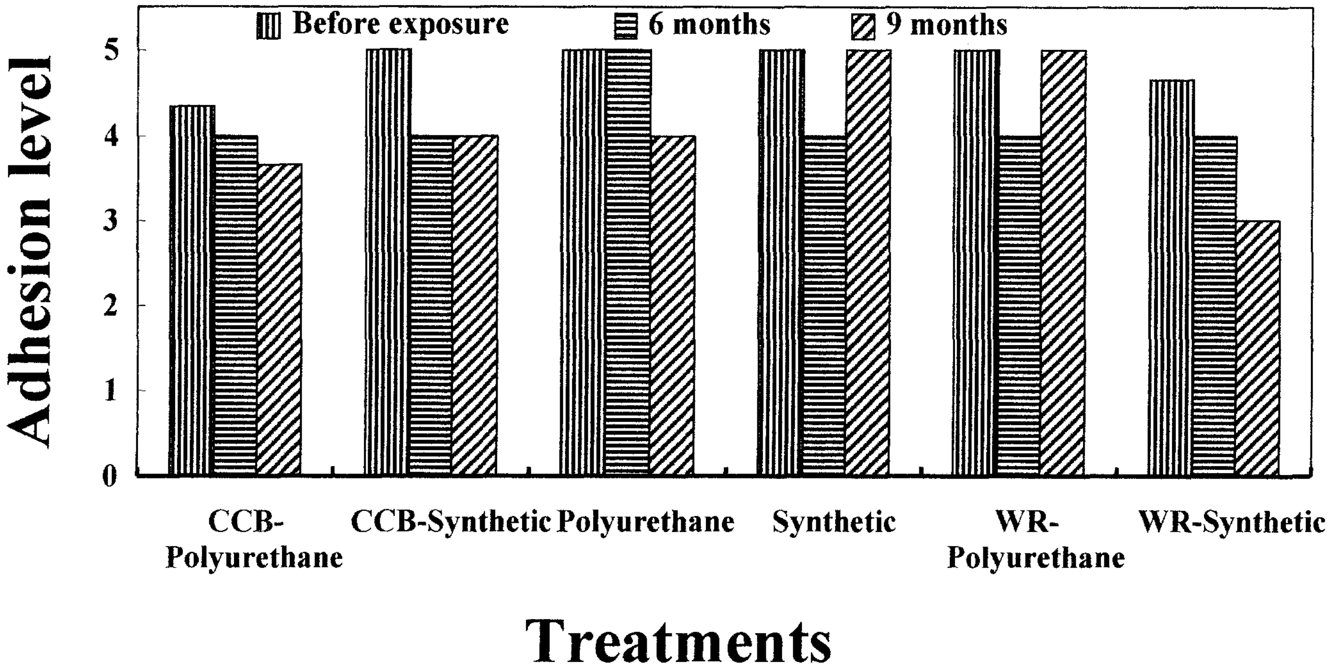

Fig. 4. Adhesion of varnish film to the chestnut surface exposed to weathering

Because cleanliness from any contaminants that interfere with the uniform response of the surface to the treating chemicals is important for an effective response of treatment that stabilizes wood.[26]

On the other hand, WR impregnation contributed to adhesion of synthetic varnish to the Scots pine panels, whereas gradual adhesion loss was observed in the chestnut panels over by time, contrary to expectation (Figs. 3, 4). The different behaviors of varnishes might be explained by their relative photoelasticity (stress and strain optical sensitivity) under various environmental conditions, creating three-dimensional stress within the coating layer and affecting adhesion of the coating layer to the applied surface.[38] Further weathering can clarify the roles of CCB and WR in the adhesion performance of the coating layer.

Water repellence

Values for water diffusibility through untreated and treated surfaces are given in Figs. 5 and 6. Chestnut wood has been more repellent than Scots pine before and after 6 months of exposure owing to its higher density and structural difference. However, that level of repellence was not permanent, and wood became more absorbent by weathering during the following period, indicating the vitality of coating for protection of wood against water and water-attracted biological agents. On the other hand, reduction in water droplet spread on untreated Scots pine was an indicator of early degradation of hemicelluloses and cellulose (the primary components of the cell wall responsible for water absorption[39]) due to erosion effects of weathering. Following the period of weathering the wood underneath the surface was exposed to further degradation, resulting in more water absorption (Figs. 5, 6).

Varnish coating significantly reduced the water diffusibility of wood within a given time. Water diffusibility through coated surfaces was similar for both varnish types along with exposure. CCB impregnation did not cause any significant increase in droplet spread compared with the other treatments within the same period of exposure. Therefore, adhesion loss of CCB-impregnated wood cannot be directly attributed to potential water attraction of CCB as an inorganic salt composition, as discussed above. Interestingly, WR impregnation had no additional contribution to the exclusion of water from wood after 9 months of outdoor exposure.

Mass loss

All the applied treatments protected the panels against fungal attack, and there was no major mass loss. In contrast, untreated panels lost up to 7% of their weight after 9 months' exposure (Figs. 7, 8). Chestnut was relatively more durable at the beginning of weathering because of its polyphenolic extractive content and high density,[6,25] but it was still degradable (Fig. 8). Thus, the weathering resistance of surfaces of naturally durable species seem limited to an early weathering period unless protected with coating. In contrast, mass loss levels remained less than 0.5% for all treated panels. Aforementioned adhesion loss of the coatings on CCB-impregnated wood surfaces caused no visible coating failure. Macroscopically, 12 test specimens from each treatment showed that 10 Scots pine and 4 chestnut control panels (untreated, noncoated) had undergone sur-

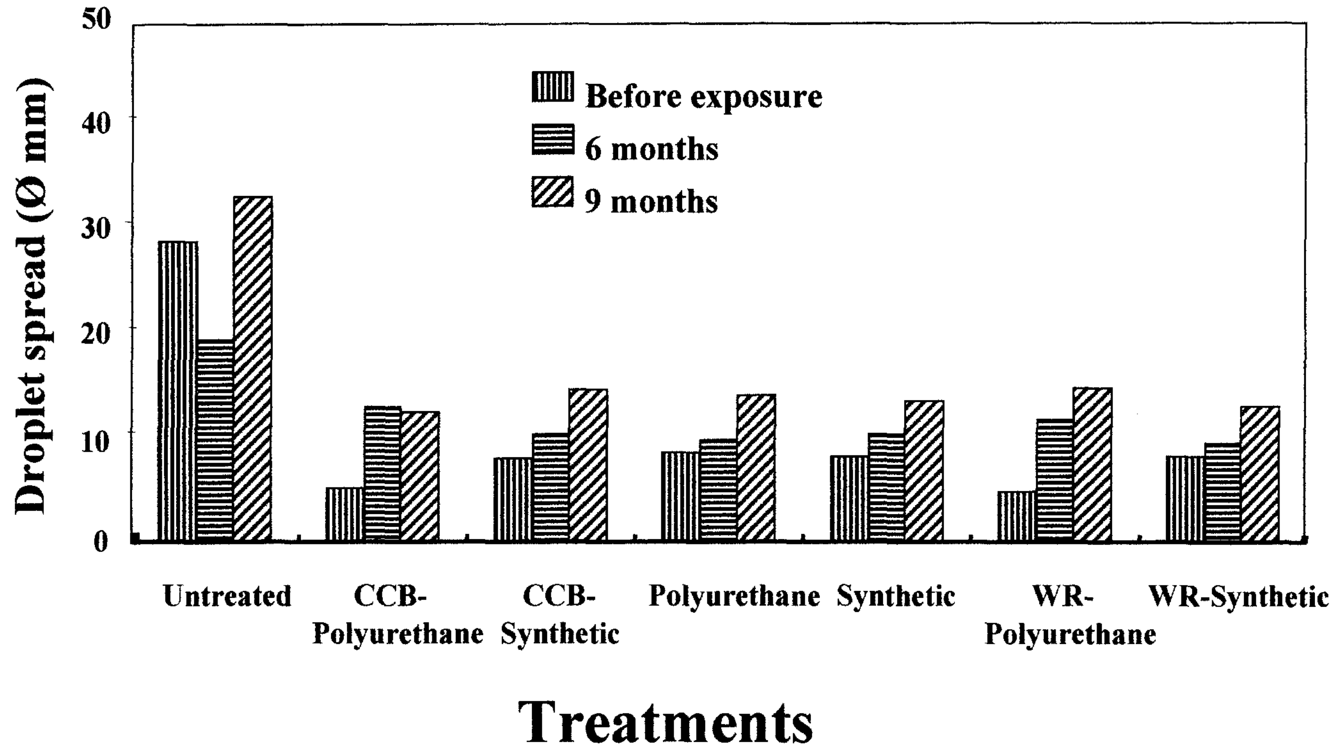

Fig. 5. Water spread diameter on coated and noncoated Scots pine surface exposed to weathering

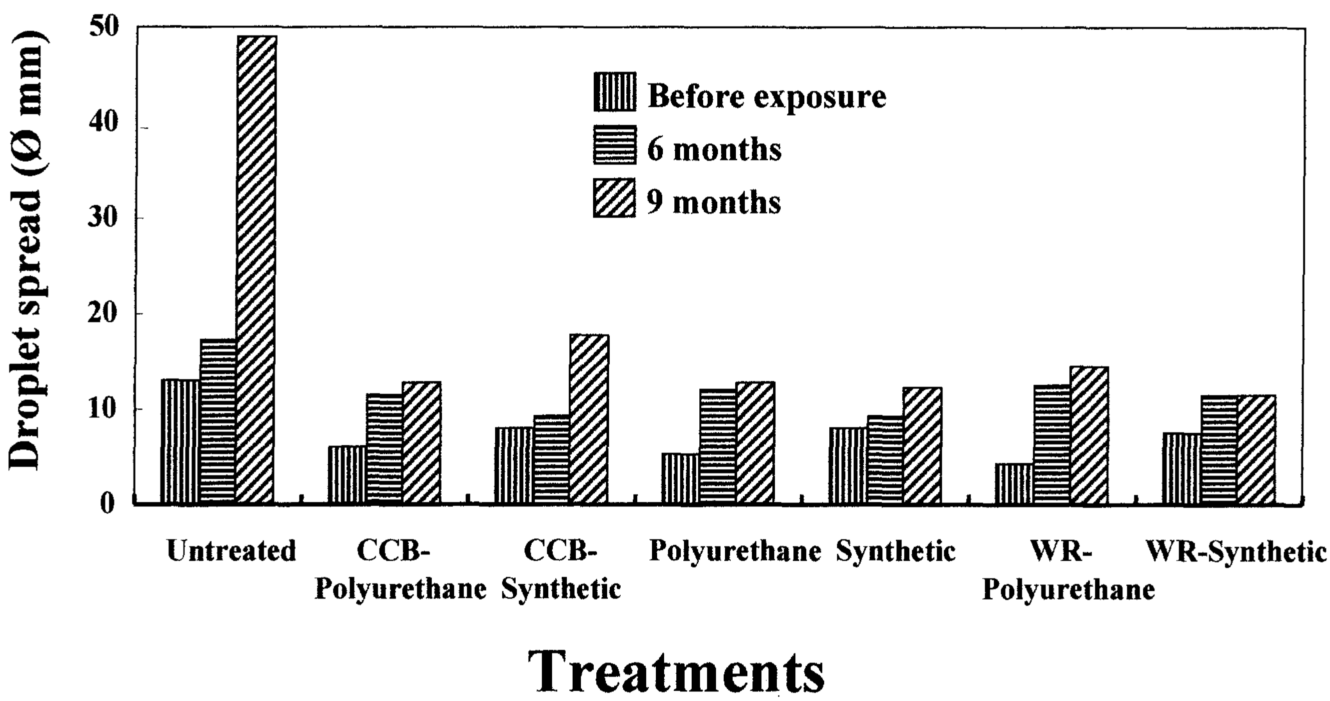

Fig. 6. Water spread diameter on coated and noncoated chestnut surface exposed to weathering

face erosion, such as flaking; and two of the Scots pine specimens had some resin bleeding after 6 months' exposure, but no mold, decay, or visible deformation was observed on the treated wood surface of either species.

Discoloration was accompanied by extensive surface degradation of all untreated control panels after 9 months of exposure, whereas only two or three of the synthetic varnish-coated Scots pine panels showed some small cracks,

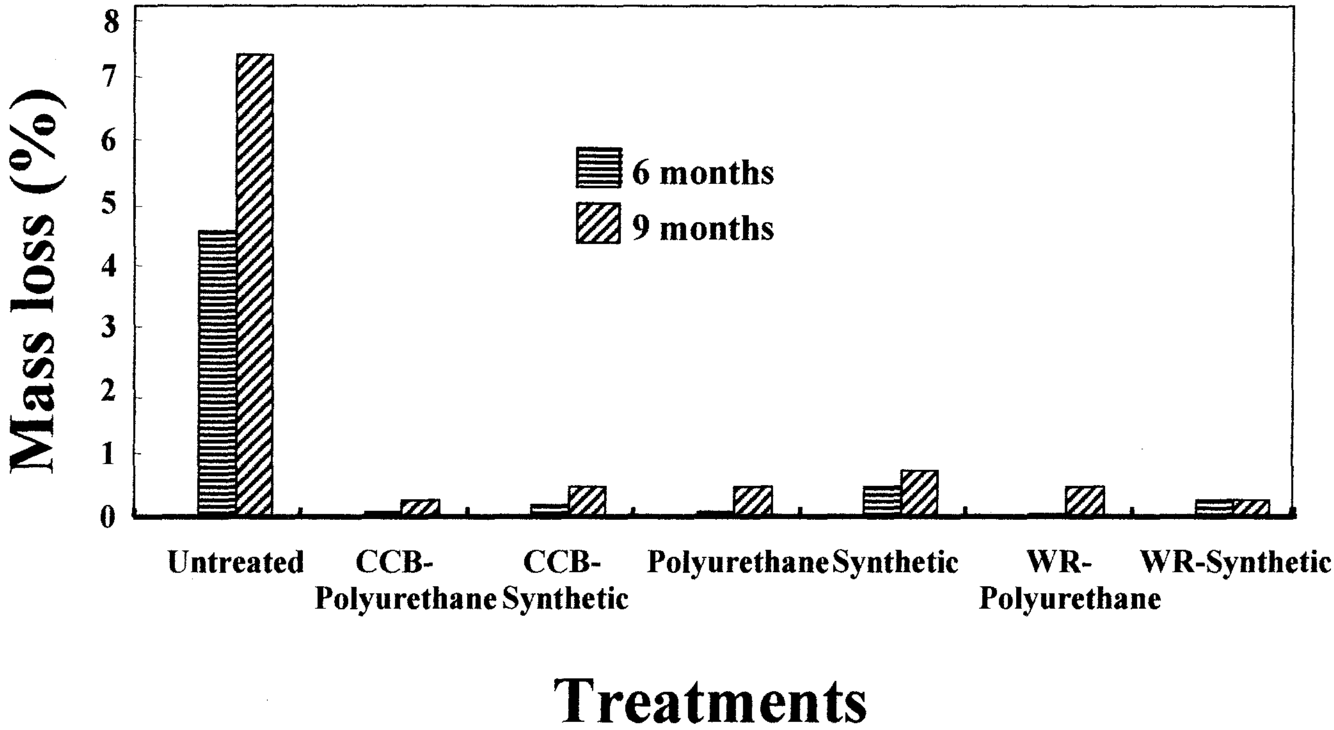

Fig. 7. Mass loss of coated and noncoated Scots pine panels exposed to weathering

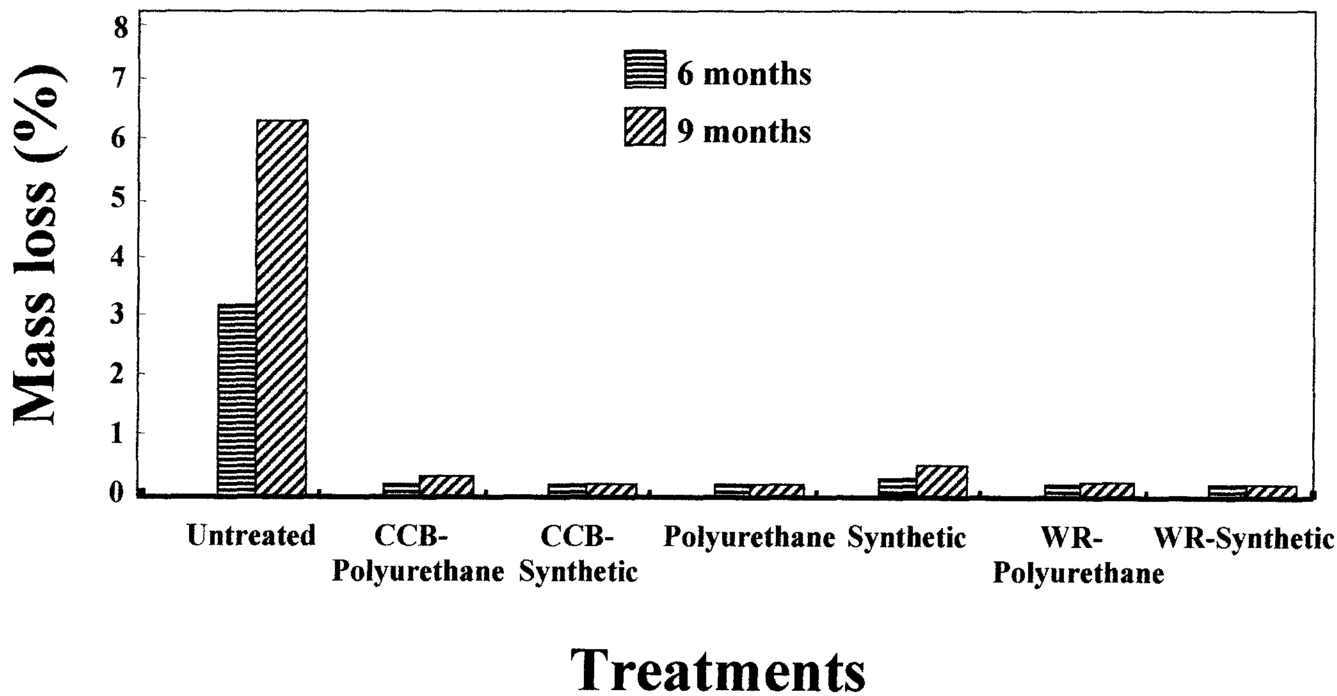

Fig. 8. Mass loss of coated and noncoated chestnut panels exposed to weathering

peeling, and local discoloration of the surface that well demonstrated the better weathering performance of CCB- or WR-impregnated panels. This was not the case for chestnut, which can be explained by the distinction of photoelastic properties of varnish types on different substrates.[38]

Surface hardness

Surface hardness values are shown in Figs. 9 and 10 for unexposed and exposed panels. Weathering softened the untreated specimens of both wood species. In contrast, all

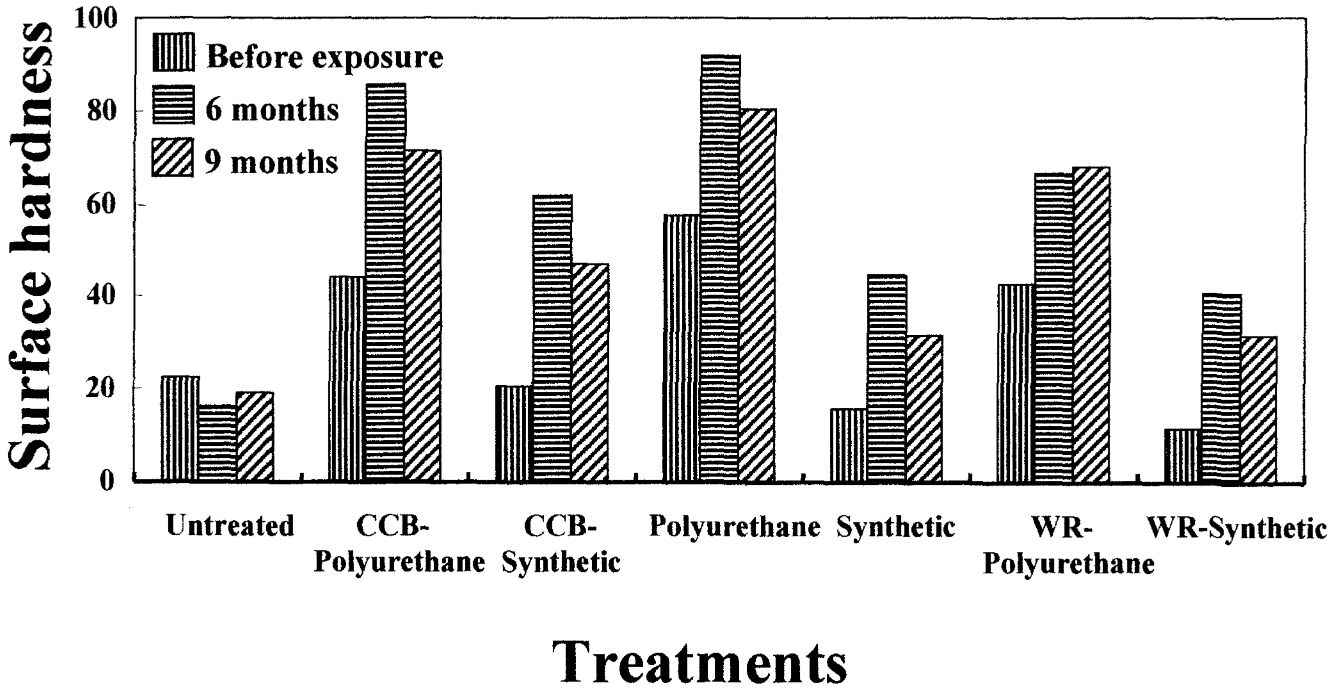

Fig. 9. Surface hardness of coated and noncoated Scots pine panels exposed to weathering

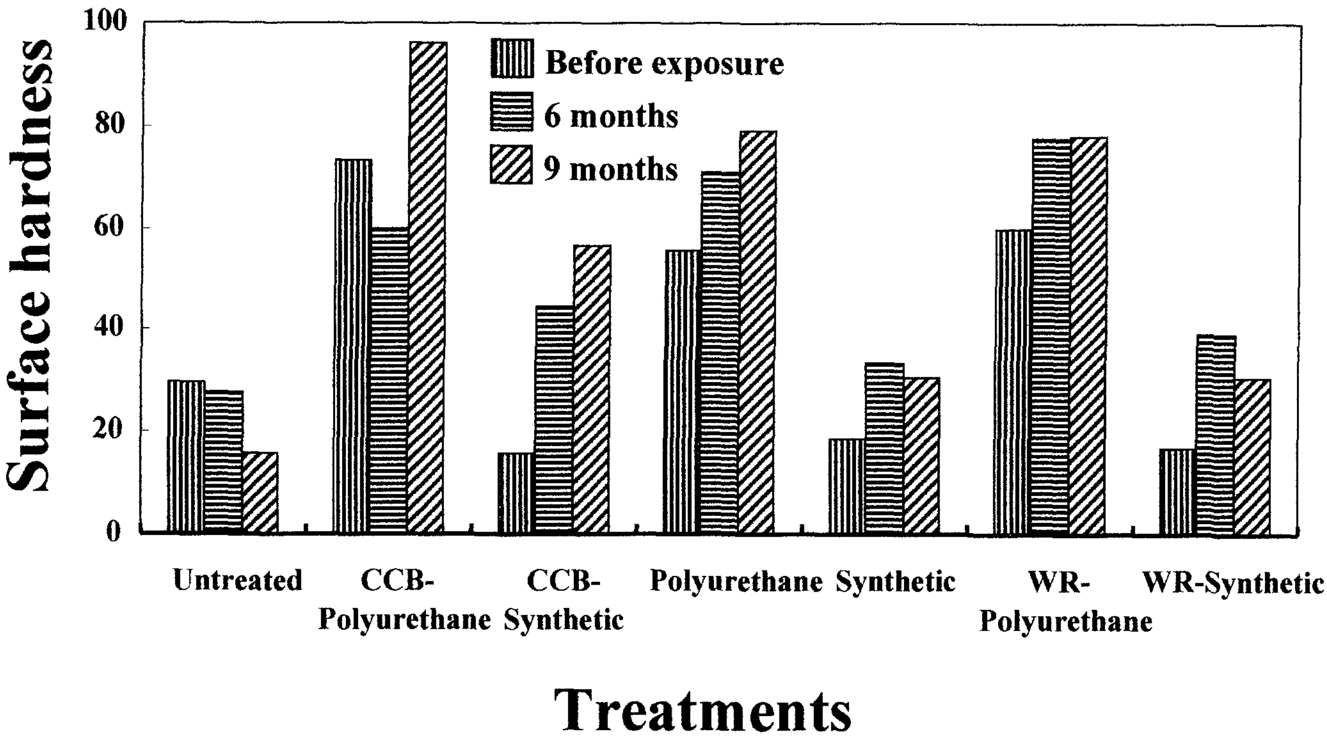

Fig. 10. Surface hardness of coated and noncoated chestnut panels exposed to weathering

the treated surfaces, upon weathering, hardened markedly up to a point and then underwent a stable phase or gradual softening. On aging, with a reduction of solvent content (by evaporation or further polymerization), the film toughness passes through a maximum with time and then degrades at a rate influenced by the environmental conditions.[26] CCB had a contributory effect on the hardness of coated surfaces. Polyurethane-coated wood appeared suitable for the conditions under impact loads, which confirmed the findings of Athawale and Bhabhe[40] and Blumstein.[38] The aliphatic nature of the isocyanate of the two-component type of polyurethane used was expected to yield additional flexibility and high film strength, enabling the varnish layer to withstand seasonal changes for long periods without failure.[41–43] Although exterior wood coatings do not need to be as hard as those used for floors, they must hold up under severe weathering conditions.[30] As a consequence, the CCB–polyurethane combination seemed to meet this requirement in reference to the recorded hardness levels (Figs. 9, 10).

Synthetic varnish-coated surfaces became softer than polyurethane-coated or even untreated wood before weathering. However, remarkable increases in hardness were recorded after outdoor exposure. This change can be explained by progressive crosslinking of alkyd molecules on exposure, followed by degradation reactions.[34] The hardness of alkyd coatings is a function of their formulations and can be improved by additives, as they are compatible with many other resins. Variations in formulations are also possible to obtain with alkyd coatings over a wide range of properties.[42,44]

Conclusions

The coating performances of a polyurethane varnish and an alkyd-based synthetic varnish produced commercially and applied over untreated or CCB-impregnated Scots pine and chestnut panels were tested for 9 months outdoors. WR-impregnated wood using the same varnish solution as the coating with some paraffin was also examined. CCB impregnation imparted high color stability when coated with either varnish. Conversely, it caused some loss in glossiness of the varnish layer coated on Scots pine but not that on chestnut, which was attributed to the light absorption and dispersion effect of the salt crystals deposited in the large lumens of the wide earlywood sections within grains. Limited adhesion loss was encountered with CCB impregnation, but it was not due to the potential water attraction of this inorganic salt composition. A superficial cleaning process applied to treated wood prior to coating is suggested to improve glossiness and adhesion. WR-coating combinations generally performed better in terms of color stability than single-coat applications. Wood attains long-term surface stability if the impregnated varnish acts as a protective multilayer film. Treated wood surfaces hardened, whereas the untreated wood softened with weathering. Polyurethane-coated surfaces were harder and more stable than those coated with synthetic varnish, before and after weathering. Mass loss of treated wood panels remained at negligible levels for both wood species, and some macroscopically visible failure occurred on coated films over a few panels after weathering, whereas untreated panels tended to discolor, crack, and flake on the surface. In conclusion, CCB impregnation greatly stabilized surface color but tended to affect the glossiness of the varnish layer on light-colored wood in addition to slow weakening of adhesion of the varnish film. The coating performance on CCB-impregnated wood should be more accurately assessed after long-term exposure. Future work should be undertaken to establish leach- and weather-resistant acetate polymer formation on wood surfaces based on the reactions between phenolic groups of wood lignin–chromium complex with borates, relative to clear coatings.

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