Improvement of the durability of clear coatings by grafting of UV-absorbers on to wood

M Kiguchi,[1] P D Evans,[2] J Ekstedt,[3] R S Williams,[4] Y Kataoka[1]

[1] Forestry and Forest Products Research Institute, Tsukuba, Japan
[2] University of British Columbia, Vancouver, Canada
[3] Swedish Institute for Wood Technology Research, Stockholm, Sweden
[4] USDA Forest Products Laboratory, Madison, USA

Summaries

Improvement of the durability of clear coatings by grafting of UV-absorbers on to wood

The photochemical resistance of polymers can be improved greatly by using grafted photostabilisers. This method was used here to improve the photostability of wood and the performance of clear coatings on wood. Reactive UV absorbers (UVAs), including 2–hydroxy-4 (2,3-epoxypropoxy) benzophenone (HEPBP) and some epoxy-functionalised triazine-type UVAs, were synthesised and the reaction conditions required to graft UVAs on to wood were examined. Grafting of reactive UVAs was more effective than UVA treatments without grafting or than chromium trioxide modification for restricting losses in weight and tensile strength of thin wood veneers during weathering. Grafting UVAs on to wood reduced photochemical changes at exposed wood surfaces and greatly improved the performance of clear coatings on modified veneer surfaces.

L'amélioration de la durabilitié de vernir clairs par le greffage des absorbants UV aux surfaces de bois

La résistance photochimique de polymères peut être largement augmentée par l'emploi de photostabilisants greffés à la surface des bois. Cette méthode était utilisée en vue d'améliorer la photostabilité de bois et en même temps le rendement de vernis clairs sur les surfaces de bois. On a synthésisé des absorbants UV réactifs (UVAs) y compris 2-hydroxy-4(2,3-époxypropoxy) benzophénone (HEPBP) et certains UVAs du type triazine époxy-functionalisé et on a étudie les conditions nécessaires pour effectuer le greffage au bois des UVAs. Le greffage d'un UVA était plus efficace que de traitement par UVA sans greffage ou par modification avec le trioxide de chrome pour limiter les pertes en poids et de la force de tension d'un placage mince au cours d'une exposition aux intempéries. Le greffage de UVAs sur bois reduit les changements photochimiques aux surfaces de bois exposées et améliore largement le rendement de vernis clairs sur les surfaces vernis après leur modification.

Verbesserung der Dauerhaftigkeit der Klarlacken durch die Einfugung der UV-Absorber in Holz-Oberfläche

Die photochemische Bestänndigkeit der Polymeren lässt sich durch das Aufpfropfen der aufgepfropften Photostabilisatoren stark verbessert. Diese Methode wurde von die Photostabilität des Holzes und die Leistung der Klarlacken auf Holzüberflächen zu verbessern. Reacktive UV-Absorber (UDAs) mit 2-Hydroxy-4(2,3-epoxypropoxy)benzophenon (HEPBP) und einige epoxyfunktionisierte Triazosorten der UVAs wurden die Reaktions-bedingungen notwendig die UVAs aufzupfropfen synthesisiert und untersucht. Aufpfropfen den reaktiven UVAs war wirksamer als UVA-Behandlung ohne Aufpfropfen oder durch Chromtrioxid, Gewichts und Zugfestigkeitsverluste der dünnen Holzfurnieren wahrend Aussenbewitterung. UVAs aufgepfropf dem Holz stark verbessert die Leistung der Klarkacke auf modifierten Furnieroberflächen.

For correspondence contact

M Kiguchi

Wood Chemistry Division, Forestry and Forest Products
Research Institute, PO Box 16, Tsukuba, Norin, Ibaraki
305–8687, Japan

Tel: +81 298 73 3211 ext.536 E-mail: mkiguchi@ffpri.affrc.go.jp
Fax: +81 298 73 3797

Introduction

Lignin in wood absorbs strongly ultraviolet light, and this leads to radical induced depolymerisation of both lignin and cellulose[1] at wood surfaces. Clear finishes perform badly on wood during exterior exposure due to degradation of the underlying wood substrate, and it has been concluded that the route to increasing the performance of such finishes lies in the photostabilisation of wood before application of the finish.[2] To-date the most effective method of preventing the photodegradation of wood involves treatment with aqueous solutions of inorganic salts, particularly hexavalent chromium compounds.[3,4] Pretreatment of wood with hexavalent chromium compounds produces a brown colouration initially, which slowly changes to green during natural exposure. Thus, it has been unacceptable to use chromium trioxide as a pretreatment to enhance the durability of clear finishes when it is essential to retain the natural appearance of wood. Also health concerns about the use of hexavalent chromium have discouraged commercial development of this concept.

At the present time there are few effective, safe, colourless pretreatments that stabilise wood against the effects of weathering and that improve the performance of clear finishes. One of the most effective methods of stabilising photolabile, synthetic, polymers when they are subjected to exterior exposure or aggressive environments is to bond chemically or graft stabilising chemicals, including UV absorbers or antioxidants, to the polymer.[5–7] The authors demonstrated that grafting of the reactive UV absorber, 2-hydroxy-4 (2,3-epoxypropoxy)-benzophenone (HEPBP) on to wood reduced the erosion of unfinished wood specimens and, as a pre-treatment, improved the performance of clear finishes during accelerated weathering.[5,7]

The aim of this study was to gain a greater understanding of the potential of UVA grafting as a photoprotective treatment for wood. Work was undertaken also to confirm the previous observation that, when used as a pre-treatment, grafting improves the performance of clear finishes on wood during weathering. The ultimate aim of the work being carried out in these laboratories is to develop photoprotective treatments that will greatly enhance the durability of natural finishes on wood.

Experimental procedures

Wood veneers

Wood blocks measuring 100 mm (longitudinal) x 50 mm (tangential) x 20 mm (radial) were cut from air-dried boards for the following species: Scots pine (*Pinus sylvestris* L), sugi (*Cryptomeria japonica* D DON) and yellow poplar (*Populus* sp). Veneers cut from the different woods were used to assess the effect of reaction conditions on grafting of HEPBP on to wood. Also these veneers were used to examine the ability of HEPBP to photostabilise wood. The air-dry density of the Scots pine, sugi, and yellow poplar specimens averaged 0.62, 0.38 and 0.46 g/cm^3 respectively. The thickness of veneers was approximately 0.085 mm. For examination of the effect of reaction conditions on percent grafting with triazine-type UV absorbers, sliced hinoki (*Chamaecyparis obtusa* ENDL) veneers (Hokusan Co Ltd, Japan, 0.20mm thickness) were used.

Chemical treatments

The benzophenone-type UV absorber, 2,4 dihydroxy benzophenone (DHBP, Lancaster Synthesis, England) was reacted with epichlorohydrin (Katayama Chemical, Japan) to give the corresponding glycidyl ether, 2-hydroxy-4 (2,3-epoxypropoxy)-benzophenone (HEPBP), (Figure 1) as described previously.[8] Purified HEPBP was a yellowish crystalline powder with a melting point of 100 to 102°C. Before chemical treatment, wood veneers were extracted with ethanol and benzene (1:2 v/v) for eight hours in a soxhlet apparatus and oven dried at 105°C for 24 hours. Veneers were treated by liquid phase and vapour phase reactions using a predipping method. For liquid phase reaction, batches of four veneers were put in 100ml glass tubes, and 80 ml of HEPBP in acetone and 0.04 g (0.05% w/v) of dimethyl benzylamine (DMBA, Katayama Chemical, Japan) as a catalyst was added to each tube. The concentrations of HEPBP solutions used were 0.5%, 1%, 2%, 4% and 8% (w/v).

Glass tubes were placed in a 200 ml stainless steel pressure vessel which was then immersed in a oil bath for 18 hours at temperatures which varied from 60 to 120°C. After this veneers were extracted in a soxhlet with acetone for 24 hours to remove any unreacted HEPBP. The extracted veneers were dried in an oven at 105°C for 24 hours and individually weighted. Batches of extracted veneers were also treated with chromium trioxide (CrO_3, Katayama Chemical, Japan). This involved dipping veneers in an aqueous solution of chromium trioxide (5% w/v) for ten seconds and then heating them for 30 minutes at 105°C to allow for fixation of chromium to occur.

For vapour phase reactions (Figure 2), veneers were either dipped in an acetone solution of HEPBP containing 0.5% DMBA (method II) or in a solution of HEPBP without catalyst (method I). In both cases the veneers were dipped for ten minutes in solutions kept at room temperature. Veneers dipped in HEPBP solution with 0.5% DMBA (method II), were subsequently put in a 100 ml glass tube. The tube was then placed in a 200 ml stainless steel pressure vessel which was immersed in an oil bath as described above. Veneers dipped in HEPBP solution without catalyst (method I) were put in a glass tube with 10 ml of 0.5% (w/v) DMBA acetone solution and then reacted in a pressure vessel (as above for method II).

Most of the work to-date on UVA grafting has involved HEPBP. In order to assess the effect of other grafting systems on the photostability of wood, Asahi Denka Kogyo Co Ltd (ADEKA) synthesised three different types of triazine-type UV absorbers (T-1, T-2 and T-3). Each UVA has one to three functional epoxide groups in the structures, which could potentially react with the hydroxyl groups in wood (Figure 3). Hinoki wood

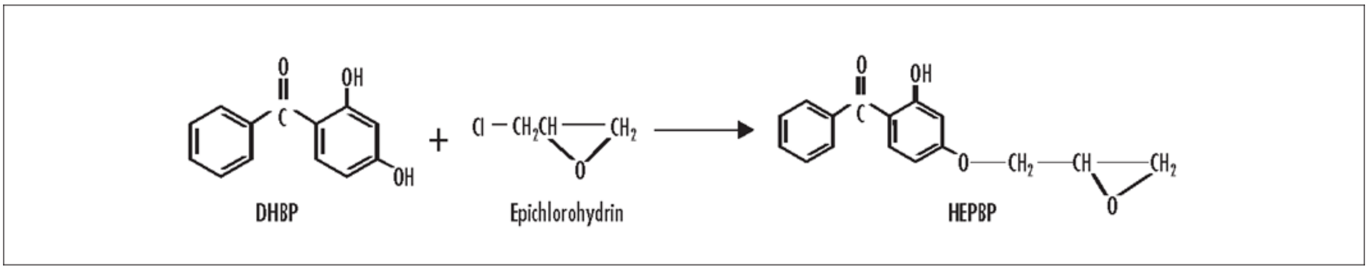

Figure 1: Synthesis of HEPBP from DHBP

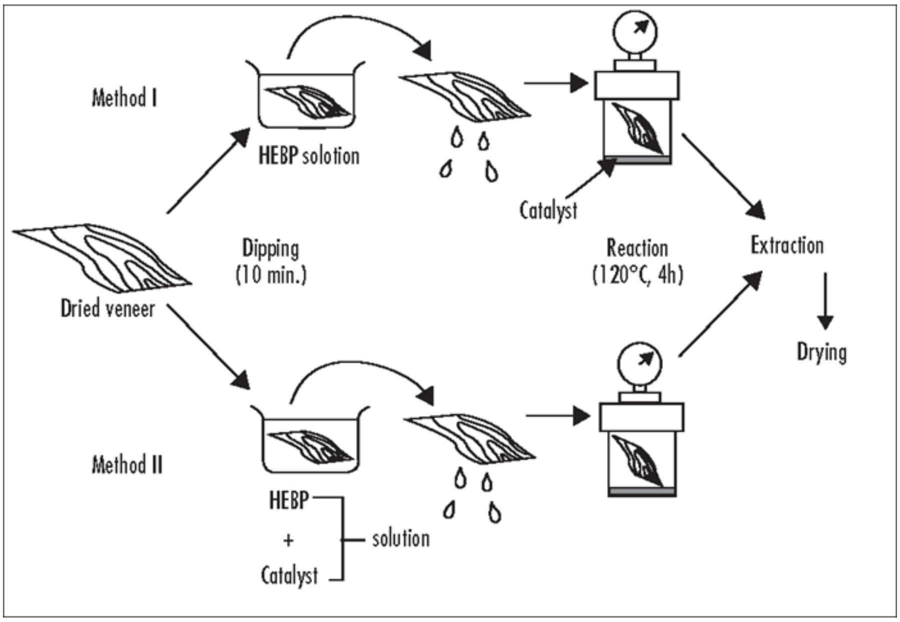

Figure 2: Vapour phase reactions of HEPBP with pre dipping methods

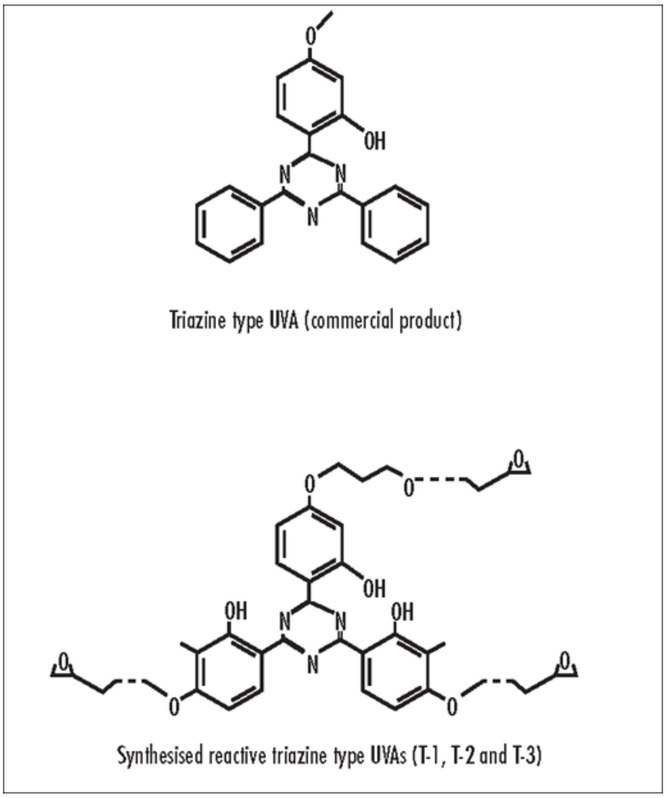

Figure 3: Synthesised reactive triazine type UVAs

veneers were reacted with these UVAs in liquid phase and vapour phase (method II) as described above. The catalyst used was DMBA in acetone at concentrations of 1% and 3% and 0.05% (w/v). Reaction temperature and time were 120°C and eight hours, respectively. After grafting, WPG was calculated based on weight of oven-dried wood veneers. The colour of the hinoki veneers became more yellow after grafting.

Weathering assessments

After treatment three kinds of veneers (Scots pine, popular and sugi) were exposed outdoors for up to 50 days facing equatorially and at an angle of 45° to the horizontal in Canberra, Australia during the summer (December and January). After weathering, veneers were oven dried as above and the weight of each individual veneer recorded. Mass losses during weathering are expressed relative to the initial treated weight. Strength tests were carried out on conditioned veneers at zero-span using a Pulmac paper tester as described previously.[9]

Hinoki veneers grafted with triazine-type UVAs were placed in an accelerating weather-o-meter (Atlas CI35A) and exposed to accelerated weathering for up to 150 hours. The accelerated weathering regime involved continuous exposure to xenon arc UV light (0.35 w/m$_2$ at 340nm), and 18 minutes deionized water spray every two hours with a black panel temperature of 63°C. Changes in the colour and mass of grafted veneers were assessed during exposure of veneers to accelerated weathering.

Instrumentation

Fourier transform infrared photoacoustic spectroscopy (FTIR-PAS: Perkin Elmer 1800 instrument coupled to a PE7500 professional computer and NTEC model 200 photoacoustic cell) was used to assess whether the HEPBP had grafted to wood components. A Minolta CR-200 colorimeter was used to quantify colour changes at veneer surfaces as a result of chemical treatments. Colour was expressed using the CIELab system (L*, a*, b*). Colour change due to treatment, Delta E* was calculated from L*, a*, b* values.

Performance of clear finishes on grafted wood

Thin wood veneer specimens measuring 140 mm (length) x 50 mm (width) x 0.3 mm (thick) were cut from commercially produced (Hokusan Co Ltd), radially sliced sugi heartwood veneer. Specimens were grafted with HEPBP, as above, to WPG of 1.5% and a similar number were grafted to WPG of 5.6%. All specimens were glued to spruce (*Picea* sp) wood blocks measuring 140 mm (longitudinal) x 50 mm (radial) x 10 mm (tangential) using an isocyanate-type adhesive (KR-134: Koyo Sangyo Co Ltd). The surface of the veneers were brush coated with an urethane primer (Kashu Toryo Co Ltd) and left to air dry for 24 hours. Specimens were then given one coat of an acrylic silicone (Woodguard; Kyushu Toryo Kogyo Co Ltd) or a polybutadiene (Viewtech fine: Saito Co Ltd) clear varnish (Figure 4). The reason for applying one finishing coat of varnish to the specimens, rather than the recommended number of two, was to assess the weathering of the clear film quickly. Coated specimens were air dried for one month and then exposed to artificial weathering in a weather-o-meter (Atlas CI35A) for 500, 750, 1000 and 1500 hours or 18 months natural weathering in racks facing south at an angle of 45° to the horizontal in Tsukuba, Japan.

After each exposure period, specimens were removed from exposure racks and coated veneer surfaces were overlaid with a 120 x 50 mm transparent grid, subdivided into 60, 10 mm^2 squares. Weathered surfaces were examined for the presence of defects, including cracking and peeling of the coating, and marked discolouration of the underlying wood. The number of squares in the grid overlying defects was counted and divided by 60 to give an expression of the resistance of the finished wood surface to weathering.[10]

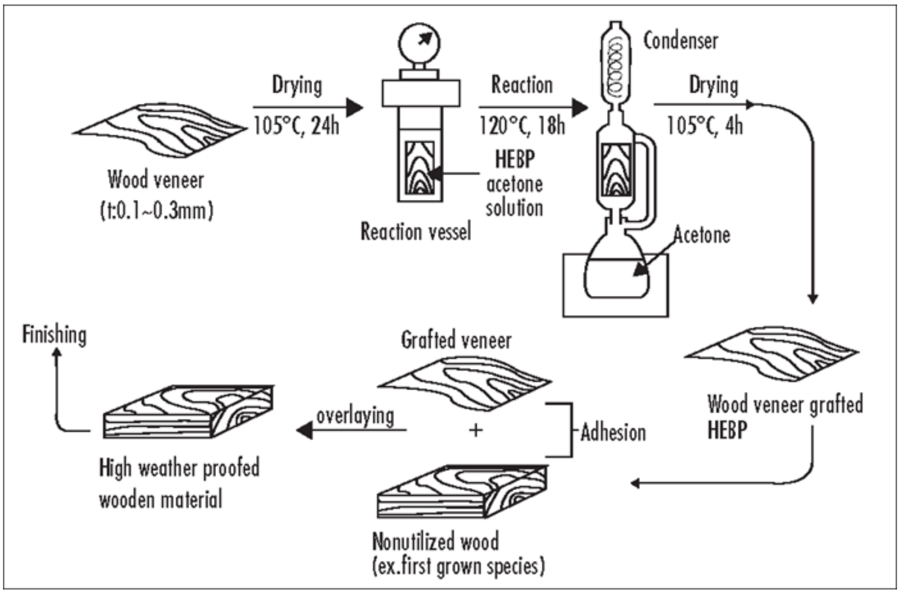

Figure 4: Preparation of UVA grafted veneer overlaid specimens for clear finishing

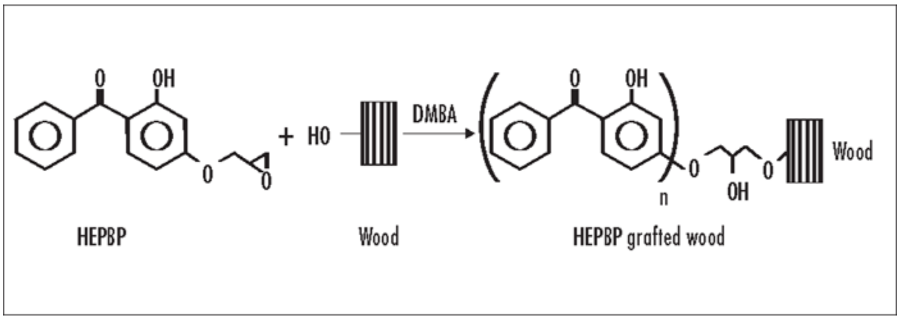

Figure 5: Grafting of HEPBP to wood by using amine catalyst

Results and Discussion

Effect of reaction conditions on grafting

At a temperature of 120°C in the presence of an amine catalyst the epoxy group of HEPBP is thought to open and react with a hydroxyl group bonding the o-hydroxybenzophenone moiety to wood (Figure 5).[5]

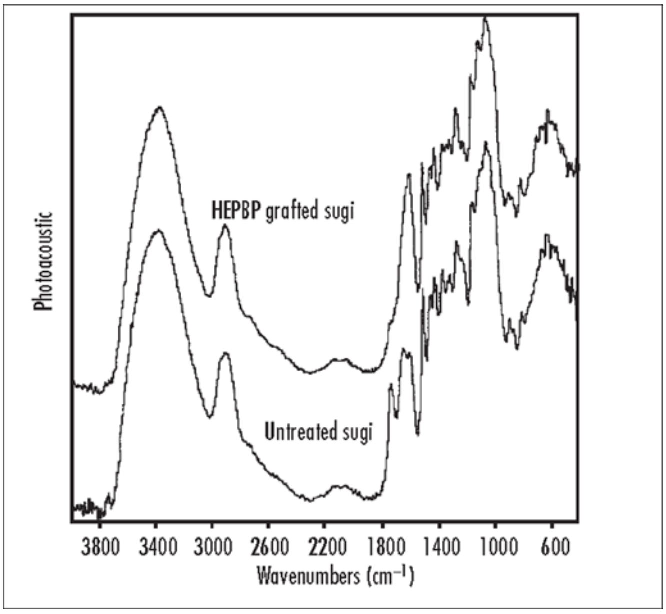

Figure 6: IR spectra of HEPBP grafted sugi veneers

Infrared spectra of grafted wood (Figure 6) showed carbonyl absorptions at 1581, 1604 and 1628 cm^{-1} due to HEPBP superimposed on the spectra for unmodified wood suggesting grafting of HEPBP to wood. Homopolymerisation of the epoxide resulting in the formation of an insoluble polymer in wood could also give rise to a similar spectrum. However, homopolymers formed from HEPBP are partially soluble in acetone and spectra of veneers were obtained after they had been subjected to prolonged (24 hours) soxhlet extraction with acetone. Taken together, the infrared spectra and the weight gains after grafting and extraction with acetone suggest that bonding of the benzophenone moiety to wood occurred. In this study, where thin wood veneers were reacted with HEPBP, it was possible to measure significant weight percent gain (WPG) after treatment and therefore examine the effect of reaction parameters on percent grafting. There was a clear relationship between the concentration of HEPBP in a solution and WPG (Figure 7) of chemical grafted to thin wood veneers. In the case of sugi and poplar, quite high WPG in excess of 8% were achieved using a solution concentration of 4%. However, a solution concentration of 8% was necessary to achieve similar WPG with Scots pine. The lower WPG of Scots pine compared to sugi and poplar are in part related to the higher density of the former since when grafting results are expressed on a mass basis, differences become less apparent, although mass increases are still lower for Scots pine. WPG and mass increases of sugi and poplar as a result of grafting were similar. There was a linear relationship between temperature and WPG for veneers reacted for 18 hours with an 8% solution of HEPBP. Below 80°C WPGs were small, but rapidly increased thereafter as the reaction temperature increased. At 120°C, which is a commonly used reaction temperature for chemical modification of wood,[11] significant WPG could be achieved. Because of this, a reaction temperature of 120°C was used for the rest of the study.

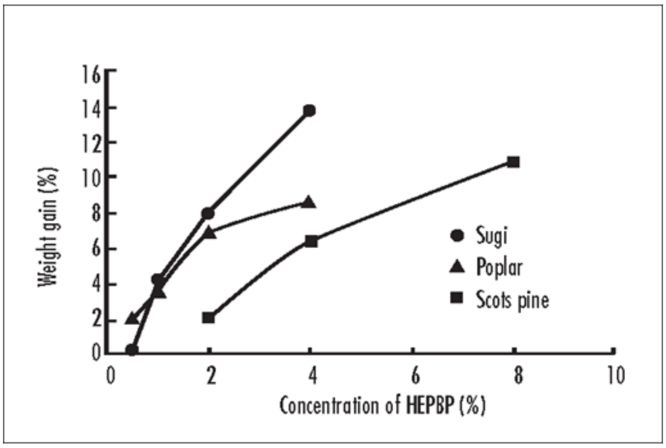

Figure 7: Relationship between concentration of HEPBP in acetone and weight gain of veneers by grafting
Reaction temperature: 120°C; Reaction time: 18h; Catalyst: Dimethylbenzylamine

Colour changes due to grafting

Treatment of veneers with DHBP caused small changes in their colour (Delta E*) (Table 1). Colour changes as a result of grafting were greater. However, grafted veneers showed significantly smaller changes in colour than veneers treated with chromium trioxide. Sugi changed from a red-brown colour to yellow as a result of grafting, as indicated by a decrease in a* and an increase in b*. Scots pine and poplar, both light-coloured timbers, also showed yellowing, ie, b* increased as a result of grafting, but there was little change in a*. Brightness values (L*) decreased slightly in Scots pine and poplar as a result of grafting.

Table 1: Colour changes in wood veneers after treatment with HEPB, DHBP or CrO_3

Wood species	*Treatment*	*Colour parameters*			
		*Delta L**	*Delta a**	*Delta b**	*Delta E**
Scots pine	Control	84.4	2.8	24.9	–
	HEPBP (11.5%)	–8.2	1.3	11.6	14.4
	DHBP (11.2%)	0.2	0.1	–0.5	0.5
	CrO_3 (5.3%)	–30.5	4.9	0.5	31.0
Sugi	Control	75.6	8.5	23.6	–
	HEPBP (14.4%)	–0.2	–4.9	8.0	9.4
	DHBP (16.3%)	2.8	–0.5	1.0	3.0
	CrO_3 (11.3%)	–25.1	–3.1	–4.7	25.7
Poplar	Control	87.3	1.5	18.0	–
	HEPBP (8.6%)	–5.8	0.0	10.6	12.1
	DHBP (9.1%)	–0.3	0.3	0.7	0.9
	CrO_3 (9.6%)	–31.4	1.0	0.0	31.4

As mentioned above, one of the reasons for the limited commercial use of chromium trioxide as a photostabilising pre-treatment for wood is that it greatly affects the colour of wood. This is clearly undesirable in a pre-treatment designed to improve the longevity of clear varnishes, since the appeal of such finishes lies in their ability to maintain the natural appearance of wood. In this respect, grafting of HEPBP is superior to chromium trioxide. Although, as a consequence of the yellow colour imparted to the treated timber, it is probably more suitable for lighter coloured joinery species such as pine (*Pinus* sp), spruce (*Picea* sp) and hinoki (*Chamaecyparis* sp) rather than darker ones such as sugi and western red cedar (*Thuja plicata* Donn ex D Don).

Mass and tensile strength losses of grafted veneers during weathering

The main technique used to assess whether grafting was effective in increasing the photostability of wood involved measurement of losses in mass and tensile strength of

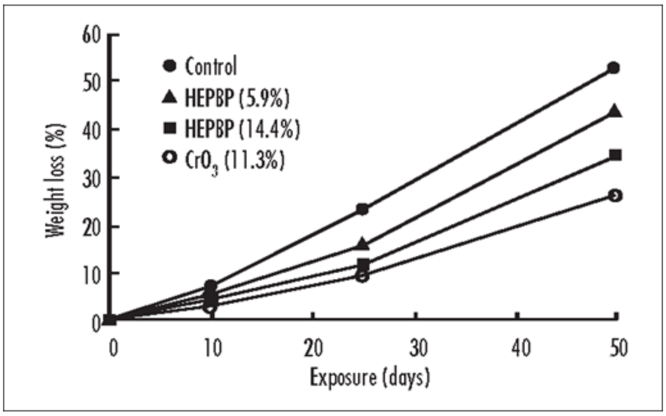

Figure 8: Weight losses (%) of HEPBP grafted sugi veneers during natural weathering
Note: Figures in parenthesis indicate the weight gain of veneers after treatment

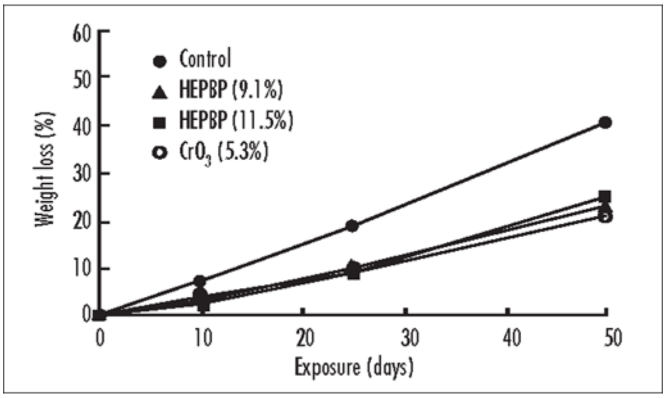

Figure 10: Weight losses (%) of HEPBP grafted Scots pine veneers during natural weathering
Note: Figures in parenthesis indicate the weight gain of veneers after traeatment

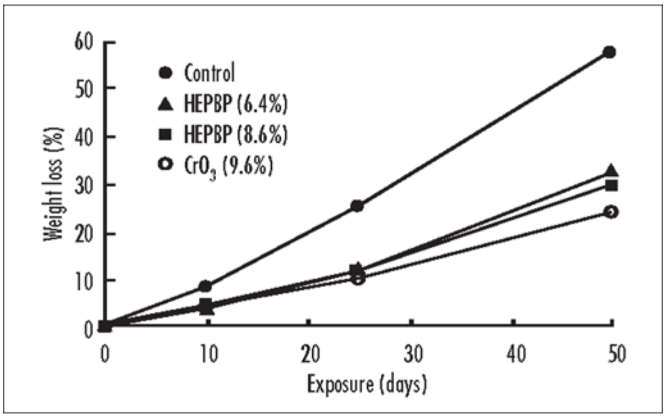

Figure 9: Weight losses (%) of HEPBP grafted poplar veneers during natural weathering
Note: Figures in parenthesis indicate the weight gain of veneers after treatment

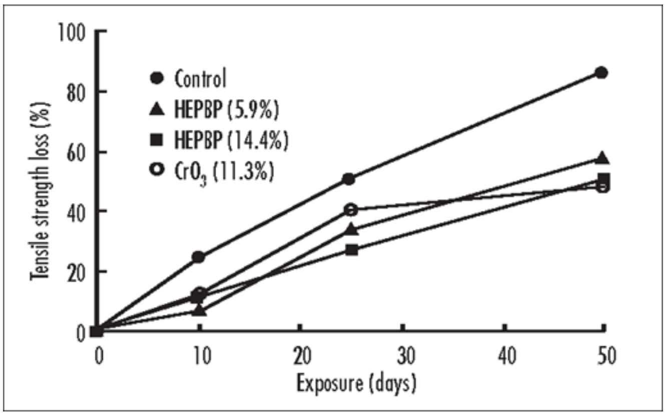

Figure 11: Tensile strength losses (%) of HEPBP grafted sugi veneers during natural weathering
Note: Figures in parenthesis indicate the weight gain of veneers after treatment

treated veneers on exposure to natural weathering. Large losses in percentage veneer mass (Figures 8 to 10) and tensile strength (Figures 11 to 13) occurred in the untreated controls during exposure. In comparison, grafting of HEPBP was highly effective in restricting losses in veneer mass and tensile strength during exterior exposure. Percentage mass and tensile strength losses of grafted veneers were generally lower in Scots pine than in sugi and poplar and this may have occurred because Scots pine was denser than sugi and poplar, and at similar percentage weight gains due to treatment, the basis by which species are compared, would contain a higher mass of grafted HEPBP than the other two species. Differences in WPG after grafting were most pronounced for sugi and this was reflected in the mass losses during exposure to the weather. Mass losses of chromium trioxide treated veneers were slightly lower than those of grafted veneers (Figures 8 to 10), but there were significant losses in the tensile strength of such veneers. This effect, which was particularly pronounced in poplar, has been noted previously[7] and arises presumably due to the oxidative depolymerisation of cellulose by chromium trioxide. Losses in the tensile strength of wood veneers during weathering occur due to the depolymerisation of cellulose and it is clear, even taking into account initial losses in tensile strength as a result of treatment, that grafting was more effective than chromium trioxide in preventing the degradation of cellulose during exposure. The finding here that, at similar weight gains, grafting of HEPBP to wood was generally as effective as chromium trioxide in restricting losses in veneer mass and superior to chromium trioxide in restricting losses in tensile strength is therefore noteworthy. Lower weight and tensile strength losses of veneers during weathering suggests that the mechanical strength and integrity of wood surfaces will be maintained for longer during exterior exposure and this should translate into improvements in the durability of overlying clear finishes.

When HEPBP is grafted to wood, benzophenone moieties are probably first bonded to lignin, since phenolic hydroxyl groups are more reactive than alcoholic hydroxyl groups.[11] This would reduce the photodegradation of lignin and cellulose by screening them from UV light. Grafting with HEPBP would therefore be expected to result in lower losses in veneer mass and tensile strength, as was observed here, since there is a good correlation between lignin and cellulose degradation and losses in veneer mass and tensile strength respectively during weathering.[9] Grafting of HEPBP because of its potential to protect both lignin and cellulose from photodegradation is clearly a superior to chromium trioxide as a photoprotective treatment for wood. However, the proven photoprotective effects of chromium trioxide on wood and the results here for grafting suggest that efficacious photoprotective systems for wood probably require covalent bonding of stabilising moieties to wood and preferably lignin.

Vapour phase grafting of HEPBP to wood veneers

In order to reduce the quantity of chemicals used in grafting, vapour phase grafting of HEPBP was attempted. Figure 14

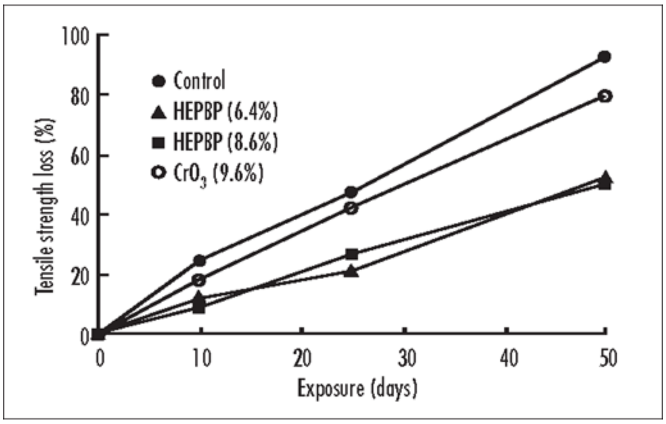

Figure 12: Tensile strength losses (%) of HEPBP poplar veneers during natural weathering
Note:Figures in parenthesis indicate the weight gain of veneers after treatment

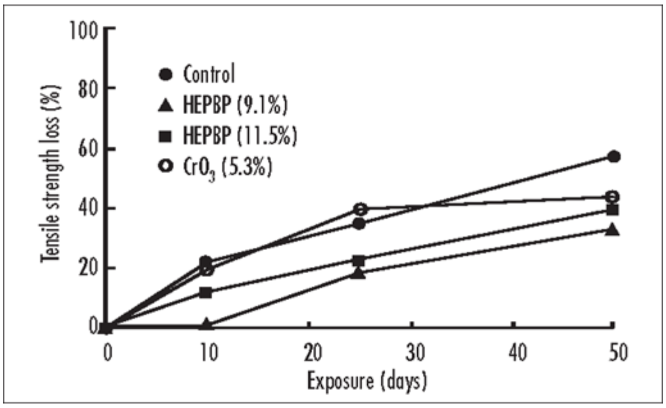

Figure 13: Tensile strength losses (%) of HEPBP poplar veneers during natural weathering
Note: Figures in parenthesis indicate the weight gain of veneers after treatment

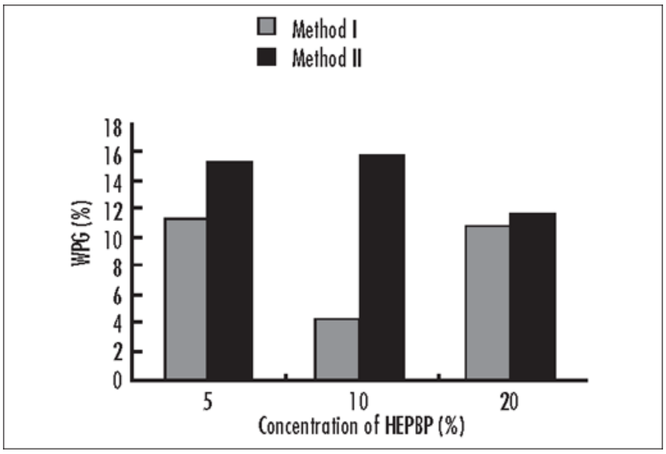

Figure 14: Weight gains of sugi veneers by vapour phase grafting with pre-dipping methods
Note: Reaction tempertaure was 120°C and reaction time was 8h

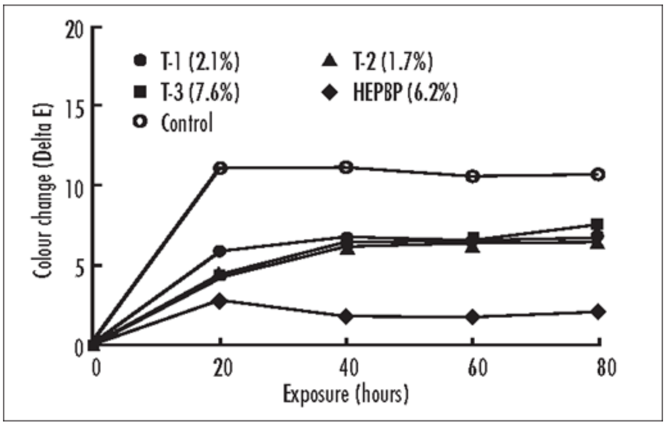

Figure 15: Colour changes in wood veneers grafted triazine type UVAs and HEPBP after xenon arc weather-o-meter
Note: Figures in parenthesis indicate the weight gain of veneers after treatment

shows WPGs after vapour phase grafting of HEPBP to sugi veneers using the pre-dipping methods. WPGs of veneers pre-treated with a HEPBP solution containing DMBA catalyst (method II) were higher than those of veneers pre-treated by only HEPBP solution and then reacted with DMBA (method I). However, WPGs of veneers using both vapour phase treatments were more than 10% when a 5% acetone solution of HEPBP was employed as the pre-treatment solution. The vapour phase method is, therefore, expected to be more economical in terms of cost of chemicals, and it also avoids the environmental problems associated with using solutions of solvents.

Grafting of triazine type UVA to wood veneers

Three kinds of reactive triazine-type UV absorbers were grafted to hinoki veneers using liquid or vapour phase reactions. The number of reactive epoxide groups in T-1, T-2 and T-3 are one, two and three, respectively (Figure 2). Table 2 shows WPGs of hinoki veneers grafted with the triazine-type UVAs and HEPBP in the vapour phase (method II). In the case of the triazine UVAs, WPG increases with concentration of UVA in solution and numbers of functional epoxide group in the UVA. However, WPG of veneers reacted with HEPBP was higher than those of veneers reacted with triazine-type UVA, despite the fact that HEPBP only contains one epoxide group.

Figure 15 shows colour difference (Delta E*) of UVA-grafted veneers after accelerated weathering. The Delta E* of veneers grafted with the triazine-type UVA was small compared to untreated control specimens; however it was higher than that of HEPBP-grafted veneer. Figure 16 shows mass losses of grafted veneers after accelerated weathering. Mass losses decreased with increasing WPG of grafted veneers. The mass losses of grafted veneers were clearly smaller than those of the untreated control specimens. These results show that mass losses of veneers grafted with triazine-type UVAs and then weathered were comparable to those of HEPBP-grafted weathered veneers. but colour changes were greater for the former.

Table 2: Weight gains of hinoki veneers grafted by reactive triazine type UVAs and HEPBP

	UVA acetone solutions	
	1%	*3%*
T-1	0.4	2.1
T-2	0.7	1.7
T-3	1.1	6.2
HEPBP	1.3	9.6

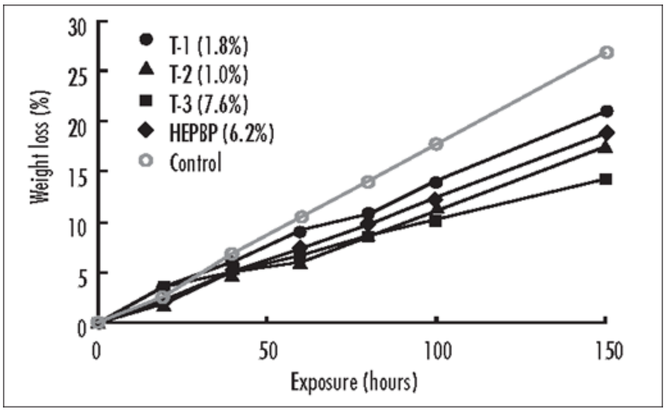

Figure 16: Weight losses (%) of triazine type UVAs and HEPBP grafted hinoki veneers during artificial weathering
Note: Figures in parenthesis indicate the weight gain of veneers after treatment

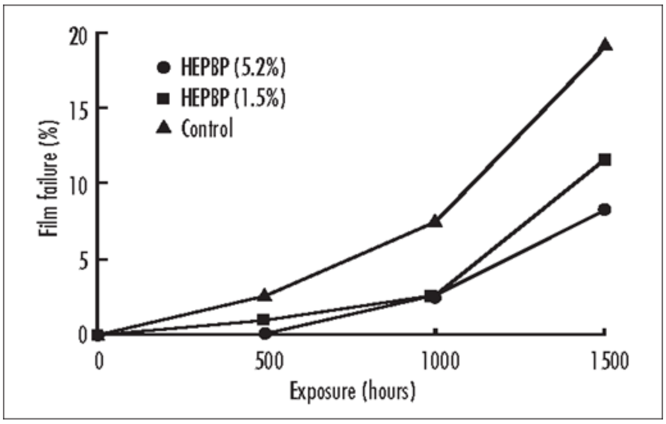

Figure 17: Film defects (%) in a silicone-urethane varnish on HEPBP grafted and untreated sugi veneer during accelerated weathering test

Performance of clear finishes on grafted wood

The precise relationship between the ability of photostabilising pre-treatments to prevent the degradation of wood veneers during exterior exposure and their effectiveness when used as pre-treatments to improve the performance of clear finishes is not known. Therefore, it was important in this study to determine whether grafting of HEPBP to wood could improve the performance of subsequently applied clear finishes during weathering. Therefore, examination of the performance of acrylic silicone or polybutadiene-based clear varnishes on grafted and untreated sliced sugi veneer during accelerated weath-

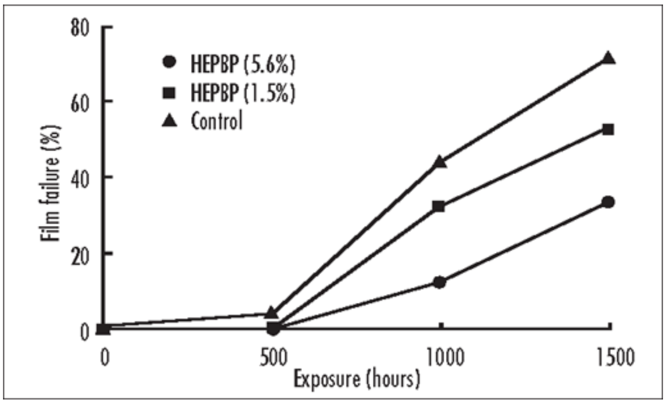

Figure 18: Film defects (%) in a polybutadiene varnish on HEPBP grafted and untreated sugi veneer during accelerated weathering test

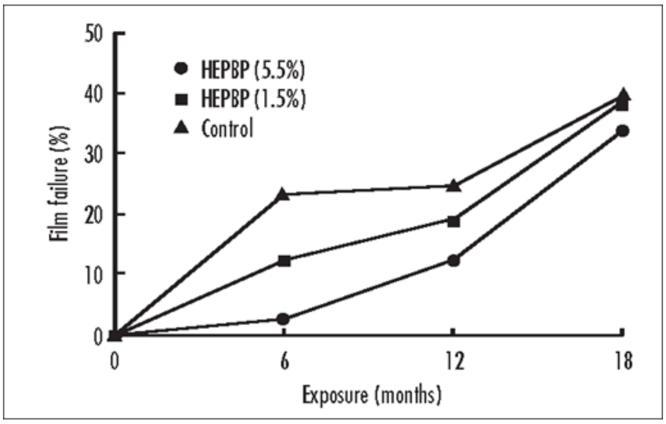

Figure 19: Film defects (%) in a silicone-urethane varnish on HEPBP grafted and untreated sugi veneer during natural weathering test in Tsukuba Japan

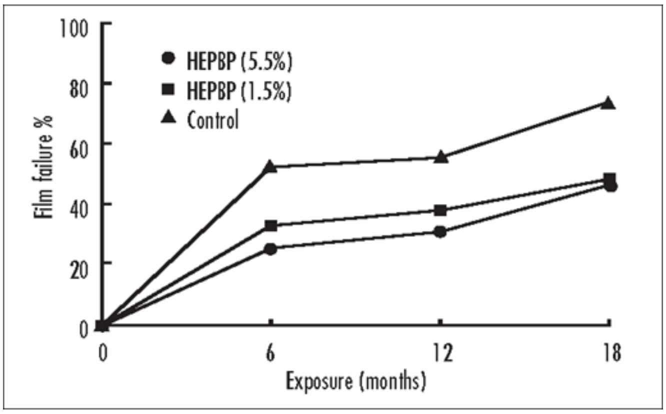

Figure 20: Film defects (%) in a polybutadiene varnish on HEPBP grafted and untreated sugi veneer during natural weathering test in Tsukuba Japan

ering was undertaken. Failure of the clear varnishes on grafted wood was significantly lower than on untreated coated controls, even for veneers grafted to weight gains of only 1.5% (Figures 17, 18). Also there was an effect of varnish type on the performance of the finishes as film failure was lower on specimens coated with the acrylic silicone varnish (Figure 17) than on those finished with the polybutadiene varnish (Figure 18).

Figures 19 and 20 show the surface failure of the clear varnishes on grafted wood during an outdoor natural weathering test for up to 18 months in Tsukuba Japan. Film failure of the silicone-urethane varnish on the HEPBP grafted veneers was initially lower than that occurring in the control in accord with results in the artificial accelerating weathering test. However, after 18 months exposure there was little difference in the percentage film failure on grafted and untreated veneers (Figure 19). In contrast, the percentage film failure of the polybutadiene varnish was still significantly lower on grafted veneers than on untreated veneers after 18 months exposure.

These results suggest that grafting of HEPBP to wood surfaces might increase the performance of clear finishes on wood during exterior exposure, possibly as a result of photostabilisation of wood surfaces beneath the clear coatings. However, these results should be regarded as tentative until confirmed by full-scale tests on grafted and coated joinery exposed to natural weathering under different climatic conditions. We have already started outdoor exposure tests of UVA-grafted and coated samples in Sweden and will start similar tests in USA, Australia and South East Asia in the near future.

Conclusions

HEPBP can be reacted with thin wood veneers resulting in permanent weight gains. Grafting of HEPBP was effective in restricting losses of veneer mass and tensile strength of all three wood species during natural weathering. Smaller differences in weight gain due to grafting of the order of 3% did not significantly influence losses of veneer mass and tensile strength during weathering. Grafting of wood with HEPBP to weight gains of only 1.5% was able to significantly improve the performance of clear finishes on wood during accelerated weathering. Grafting of HEPBP to wood was generally as effective as chromium trioxide in restricting losses in veneer mass and superior to chromium trioxide in restricting losses in tensile strength. Furthermore, undesirable colour changes arising from treatment were smaller for grafting compared to the changes caused by chromium trioxide.

Vapour phase grafting of HEPBP was attempted by dipping veneers in a solution of HEPBP and then heating veneers at 120°C in a reaction vessel. WPGs of veneers reacted in the vapour phase were similar to those achieved using a liquid phase treatment technique. The presence of a catalyst (DMBA) in the HEPBP solution instead of in the reaction vessel was more effective in promoting grafting of HEPBP to sugi veneers than when the DMBA was used in the reaction vessel.

An attempt was made to graft new triazine-type UV absorbers containing epoxide functional groups to hinoki veneers. WPGs that were achieved were similar to those of HEPBP-grafted veneers. Triazine grafted veneers also showed similar losses in mass during an artificial weathering test as HEPBP-grafted veneers, but they showed greater discolouration.

Grafting of UV absorbers to wood clearly shows promise as a means of protecting wood surfaces from photodegradation. Overlaying solid wood with a thin veneer of grafted wood, which is then coated with a clear finish, offers a unique solution to the problem of achieving durable clear wood finishes. As a commercial pre-treatment method intended to improve the performance of clear finishes on wood, grafting is unsuitable for the DIY market, but it could conceivably be used as an industrial pre-treatment method. To this end, further research is required to reduce the cost of grafting of UVAs to wood and to assess the performance of UVA-grafted and coated wood surfaces in different climatic conditions.

References

1. Evans PD, PD Thay and KJ Schmalzl, Degradation of Wood Surfaces during Natural Weathering. Effects on Lignin and Cellulose and on the Adhesion of Acrylic Latex Primers, Wood Science and Technology, **30**, 411–422, 1996
2. Derbyshire H and ER Miller, The Photodegradation of Wood During Solar Irradiation, Holz als Roh-und Werkstoff, **39**, 341–350, 1981
3. Williams RS and WC Feist, Wood Modified by Inorganic Salts: Mechanism and Properties I. Weathering Rate, Water Repellency, and Dimensional Stability of Wood Modified with Chromium (III) Nitrate Versus Chromic Acid, Wood and Fiber Science, **17**, (2), 184–198, 1985
4. Evans PD, AJ Michell and KJ Schmalzl, Studies of the Degradation and Protection of Wood Surfaces, Wood Science and Technology, **26**, 151–163, 1992
5. Williams RS, Effect of Grafted UV Stabilizers on Wood Surface Erosion and Clear Coating Performance, J. Applied Polymer Science, **28**, 2093–2103, 1984
6. Grelier S, A Castellan, S Desrousseaux, A Nourmamode and L Podgorski, Attempt to Protect Wood Colour Against UV/Visible Light by Using Antioxidants Bearing Isocyanate Groups and Grafted to the Material with Microwave, Holzforschung, **51**, 511–518, 1997
7. Kiguchi M and PD Evans, Photostabilisation of Wood Surfaces Using a Grafted Benzophenone UV Absorber, Polymer Degradation and Stability, **61**, (1), 33–45, 1998
8. Manasek Z, I Zvarai and J Luston, Synthesis of 2-hydroxy-4-(2,3-epoxypropoxy) benzophenone, J. Applied Chemistry (USSR), **49**, 1167–1170, 1976
9. Evans PD and KJ Schmalzl, A Quantitative Weathering Study of Wood Surfaces Modified by Chromium VI and Iron III Compounds, Holzforschung, **43**, 289–292, 1989
10. Kiguchi M, M Suzuki and Y Imamura, Weatherability of Exterior Wood Coatings in Japan, Conference Papers of Advances in Exterior Wood Coatings and CEN Standardisation, Brussels, Paper 12, October 1998
11. Rowell RM, Chemical Modification of Wood, Forest Products Abstracts, **6**, (12), 363–382, 1983