FTIR Studies of the Effects of Outdoor Exposure on Varnish-Coated Wood Pretreated with CCB or Water Repellents

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Scots pine (Pinus sylvestris L.) *and chestnut* (Castanea sativa Mill.) *panels were coated with a polyurethane or an alkyd-based synthetic varnish. Some of the panels were impregnated with chromium-copper-boron (CCB) or the varnishes themselves before coating, as preservative-coating or water repellent (WR)-coating combination treatments, respectively. Earlier drastic changes in the intensity of the bands assigned to lignin and their shifts to some other stretching points were mostly attributed to chemical modification of lignin with the chromium in CCB, as well as the previously reported high color stability of CCB-impregnated wood. IR spectra of the nine months of weathering indicated that the synthetic varnish coating of non-impregnated or CCB-impregnated wood limited the reactions in lignin compared with polyurethane coating. Wood density and structural difference also seemed to play an important role since changes in lignin were mostly observed after six months of exposure for chestnut wood. Therefore, chemical reactions of CCB-wood cell wall components on the surface appeared likely to be affected from varnish type (their relative absorbency and distribution of sunlight), wood species (density and extractive substances), and exposure time and conditions.*

INTRODUCTION

Although weathering does not affect the structural strength of wood,[1] changes in surface integrity severely impair the performance of exterior coatings applied to wood.[2] Many materials have been suggested as suitable coatings for wood surfaces. However, the evaluation techniques that led to these recommendations evidently were inadequate, since most materials fail, some relatively quickly, when exposed to accelerated weathering or applied to field test fences.[3] Use of unpainted wood in exterior construction has created a demand for a clear finish, which will preserve the natural beauty of wood.[4] Although transparent film-forming finishes are not generally recommended for exterior use on wood,[5] decomposition stages of, and photochemical changes on, wood surfaces coated with such varnishes have not been extensively studied in relation to performance outdoors. The primary problem is not finding or making a varnish capable of withstanding exterior exposure, but rather preventing degradation of the wood itself by UV light.[6] Therefore, treatment of wood with a chromium-containing preservative such as chromated copper arsenate (CCA) before coating was suggested to extend the lifetime and durability of the coating system.[7,8] Since environmental awareness has forced the use of environmentally safe and arsenic free chemicals for wood and wood-based composite protection,[9,10] alternatives to arsenic containing preservatives are required. As a boron-containing wood preservative, which is generally considered to have low mammalian toxicity, chromium-copper-boron (CCB) was expected to fulfill this requirement. It is believed that boron-treated wood can withstand outdoor exposure in cases of water shedding coatings.[11] But, the extent of the protective effect of different coating systems may vary. Peylo and Willeitner[12] suggested water repellent coatings over boron-treated wood to increase boron stability in wood. Various paints and finishes over Bora-Care® (U.S. EPA

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Table 1—Typical Properties of Commercial Varnishes Used

Property	Synthetic Varnish	Polyurethane Varnish
Commercial name	Polimarin boat varnish	Ekodur polyurethane varnish
Gloss 60°	Very glossy	Glossy
Solid % (as weight)	55±2	56±2
Specific gravity (at 23°C)	0.91±0.01	1.00±0.01
Viscosity	170±10 sec at 20°C (DIN 4)	40±5 sec at 25°C (DIN 6)
Thinning	Not required	Thinned with a NITRO thinner at 5 % w/w (Ekodur polyurethane thinner)
Prepare	Ready to use	Mixed with a hardener at 1:1 as volume before use (Ekodur hardener)
Production purpose	Protection of wooden parts of boats against sea water, sunlight, detergents, rain and impact loads	All wooden surfaces

Reg. No. 59905-3) treated wood panels were subjected to 3,000 hr exposure in a QUV accelerated weathering tester. No significant difference was found in overall coating performance over borate-treated wood versus performance over untreated wood.[13,14] Sell et al.[15] tested outdoor weathering durability of CCB applied on Obeche, red beech, spruce, and fir wood as surface treatment. High resistance of CCB-coated wood against weathering has been attributed to the protective effect of Cr-Cu-salt-solutions on wood surfaces.[16] Quite recently, high outdoor color stability has been obtained with the CCB-impregnated Scots pine and chestnut wood surfaces coated with a polyurethane or alkyd-based synthetic clear varnish.[17] In order to reveal the chemical changes and reasons for the reported color stability with CCB impregnation on wood surface, those clear varnishes were applied over a CCB-impregnated wood surfaces and exposed outdoors. Varnish-brushed alone or impregnated into wood as water repellent (WR) treatment surfaces were also exposed outdoors at identical conditions to determine their relative outdoor performance. Fourier transfer infrared (FTIR) spectroscopy was employed to analyze the changes of wood constituents on the surface with weathering in relation to the applied treatment systems. Results of the nine months of outdoor exposure were evaluated.

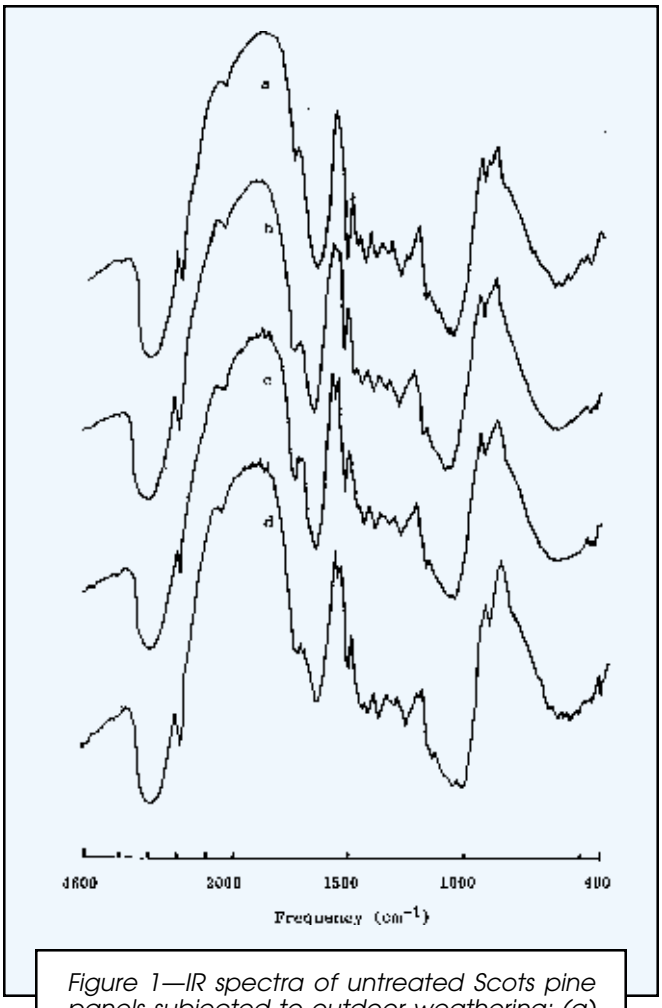

Figure 1—IR spectra of untreated Scots pine panels subjected to outdoor weathering: (a) before weathering; (b) after three months of exposure; (c) after six months of exposure; and (d) after nine months of exposure.

EXPERIMENTAL

Chemicals, Impregnation Process, and Coating Systems

Wood panels measuring 10 (radial) × 100 (tangential) × 150 (longitudinal) mm were prepared from air-dried sapwood of Scots pine (*Pinus sylvestris L.*) and chestnut (*Castanea sativa Mill.*). Oven-dry specific gravity of these species was measured as 0.49 and 0.58, respectively. Annual growth rings were arranged to make a 45° angle to the radial edge at cross-sections. CCB aqueous solution of 7.5% concentration was prepared from the dry salt supplied by Korusan Ltd. (Istanbul), composed of 25% boric acid, 36% sodium bichromate, 37% copper sulfate, and 2% non-aromatic patent additives. An alkyd-based synthetic varnish (Polimarin® boat varnish) and a two-component polyurethane varnish (Ekodur Poliuretan® bright varnish) consisting of an aliphatic isocyanate-terminated component and an active hydrogen-bearing monomer, which, when blended, cure at room temperature with the four or five hours pot life of the blend were supplied by Polisan Chemical Co. of Turkey (*Table* 1). Both varnishes were specially prepared

and supplied by the manufacturer free from any of the UV absorber or inhibitor following our request. They were applied separately over untreated and CCB-impregnated wood. They were also impregnated into the wood as water repellent (WR) solutions prepared by solving the varnishes in white spirit (20% v/v) and containing one percent 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 held under vacuum for 30 min before introducing the treatment solutions of CCB or WR. Then, they were allowed to absorb a solution at atmospheric pressure for 30 min. After impregnation, the wood panels were conditioned for three weeks at 65% RH and 20±1°C before coating. Weight gain of the specimens due to chemical loading was calculated as follows:

$$\text{Weight gain (\%)} = \frac{Wf - Wi}{Wi} \times 100$$

where Wf is the final conditioned weight of a wood block and Wi is the initial weight.

Filler was not used in order to avoid any potential interference with the glossiness and adhesion of the coating. Instead, a varnish, used as a primer coating to fill voids, was applied twice to untreated and CCB-impregnated panels. A topcoat was also applied to reveal the absolute effect of weathering through the clear varnish layers. The water-repellent was considered to function as primer coat in the WR-impregnation-varnish coating treatment system. Sufficient time for layer settling (20-25 min) was left between successive applications until reaching the target retention of 75 g/m^2 for primer and 100 g/m^2 for topcoat that was adjusted by consecutive weighing based on the solid content of the prepared solutions. Specimens were left in ambient conditions for 24 hr before topcoating, according to the instructions given by the varnish manufacturer. Surfaces were gently sanded with No. 220 abrasive paper to obtain a smooth surface prior to topcoat.

Each treatment group consisted of 12 individual panels. In total, seven groups of wood panels for each species were exposed outdoors (*Table* 2). Weathering differences between varnish-coated CCB-impregnated wood and the same wood coated with a single varnish is considered to reflect the CCB's effect on weathering durability.

Outdoor Exposure

ASTM D 358-55[18] was consulted for panel preparation for outdoor exposure. All non-coated edges and

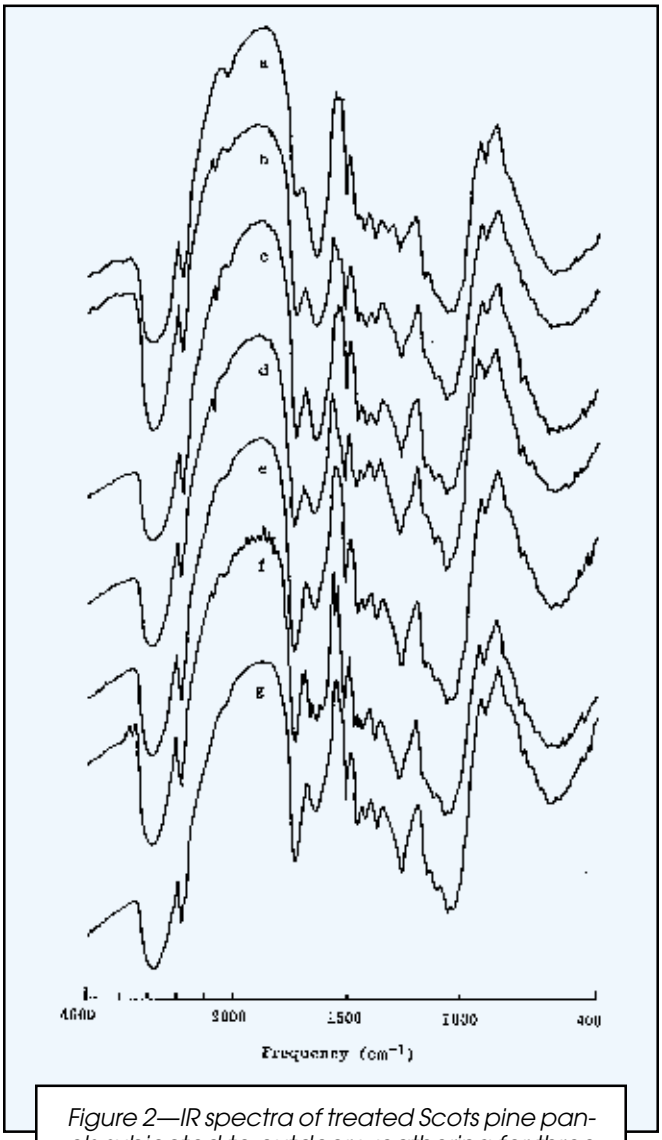

Figure 2—IR spectra of treated Scots pine panels subjected to outdoor weathering for three months: (a) non-impregnated after three months exposure; (b) CCB-treated polyurethane varnish-coated; (c) CCB-treated synthetic varnish-coated; (d) polyurethane varnish coated only; (e) synthetic varnish coated only; (f) WR impregnated with polyurethane varnish; and (g) WR impregnated with synthetic varnish.

Table 2—Treatment Systems Applied to Wood Panels Prior to Outdoor Exposure

Impregnation	Concentration	Coating System
Untreated control	—	—
CCB (chromium copper boron)	7.5% Aqueous solution	Polyurethane varnish
CCB	7.5% Aqueous solution	Synthetic varnish
WR (water repellent) treatment with polyurethane varnish	20% Solved in white spirit includes 1% paraffin wax	Polyurethane varnish
WR treatment with synthetic varnish	20% Solved in white spirit includes 1% paraffin wax	Synthetic varnish
Coating alone	—	Polyurethane varnish
Coating alone	—	Synthetic varnish

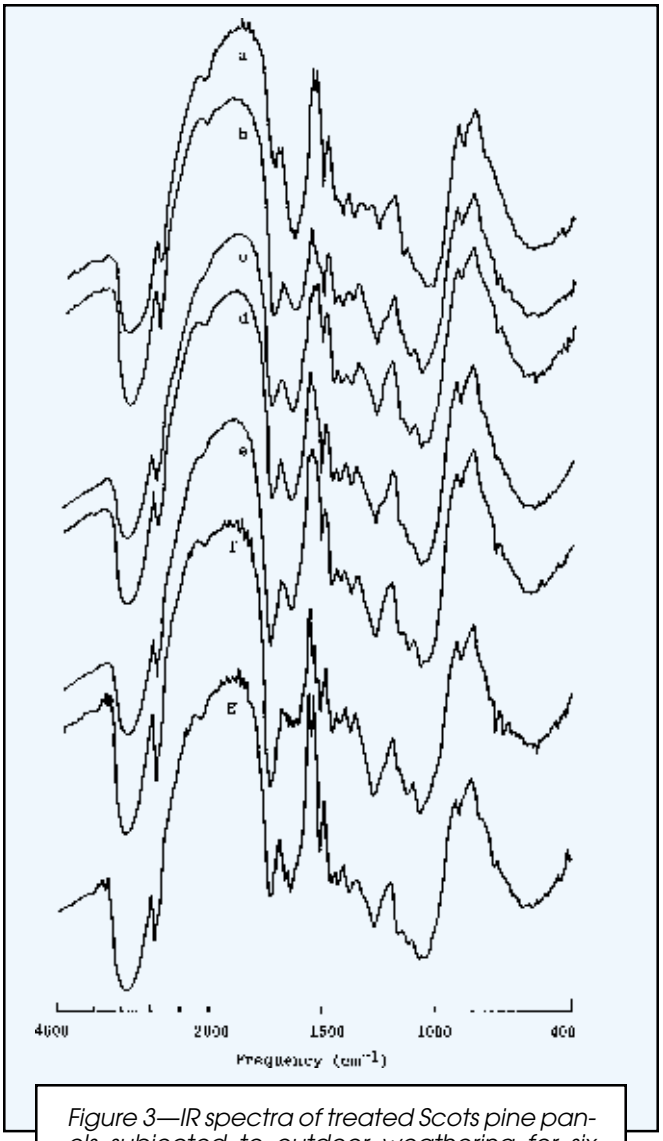

Figure 3—IR spectra of treated Scots pine panels subjected to outdoor weathering for six months: (a) non-impregnated after six months exposure; (b) CCB-treated polyurethane varnish-coated, (c) CCB-treated synthetic varnish coated; (d) polyurethane varnish coated only; (e) synthetic varnish coated only; (f) WR impregnated with polyurethane varnish; and (g) WR impregnated with synthetic varnish.

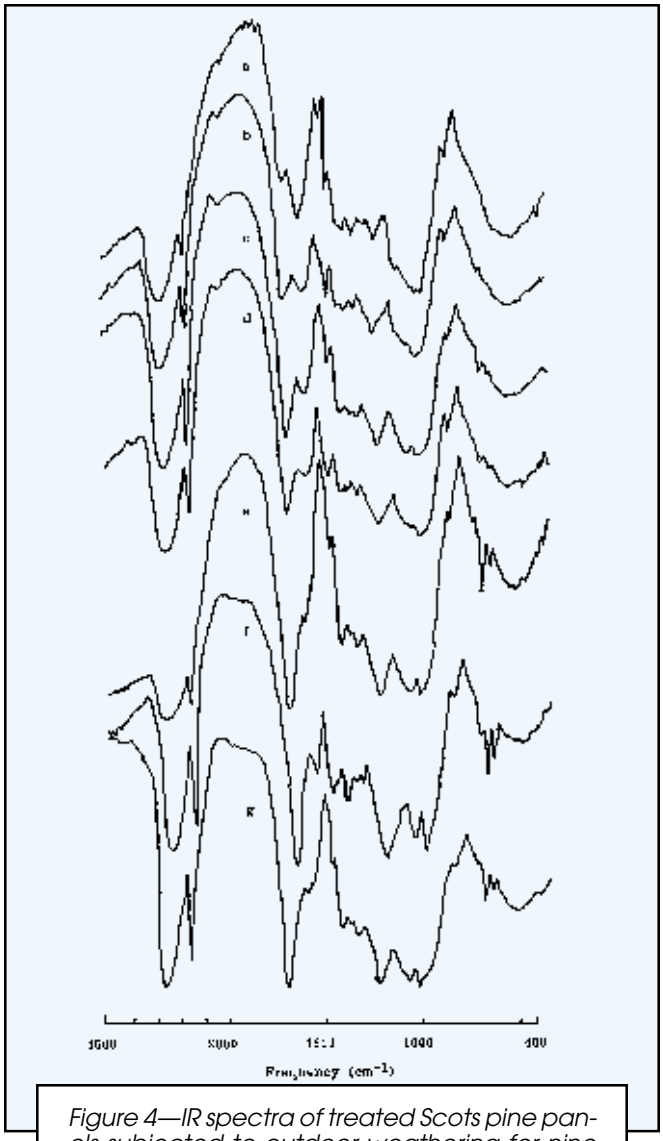

Figure 4—IR spectra of treated Scots pine panels subjected to outdoor weathering for nine months: (a) non-impregnated after nine months of exposure; (b) CCB-treated polyurethane varnish coated; (c) CCB-treated synthetic varnish coated; (d) polyurethane varnish coated only; (e) synthetic varnish coated only; (f) WR impregnated with polyurethane varnish; and (g) WR impregnated with synthetic varnish.

back sides of the panel were sealed with a polyamide-cured epoxy resin prior to exposure at 45° south on their tangential surfaces on the wooden decks, which were installed 50 cm above ground. Direct contact between the specimens and the wooden frame was avoided by wrapping the frame smoothly with aluminum foil. Since the outdoor weathering process is closely related to the climatic conditions of the location where the wood is exposed,[19] a test site was established near the Regional Meteorological Observation Station in the Black Sea region at Trabzon (a coastal city of Turkey located at 41.00° North and 39.43° East), to enable practical assessments. Climatic data of the test site during the exposure periods from June 1996 until March 1997 were recorded.

Infrared (IR) Spectral Analysis

FTIR-IR spectroscopy, which is capable of detecting chemical changes on a wood surface to a depth of approximately 0.13 to 2.15 μm,[20] was used to determine the loss or changes in lignin during weathering. Frequency intervals of spectra were evaluated between 1200 and 1800 cm^{-1} in which changes in lignin generally are reflected.[21] Band assignment was made according to the range of maxima given by Faix.[22] Other related works were also considered for general assignment of obtained peaks (*Table* 3).[23-33]

IR spectra were taken from the powder of wood sampled beneath the film layer of varnish coatings for

Table 3—Band Assignment for Exposed and Unexposed Wood Panels Between 1200 and 1800 cm^{-1}

Band Number (cm^{-1})	Assigned Band Origin	Reference Number
1230	C-C Plus C-O plus C=O stretching	22
1270	C=O Stretching	22, 25
1330	Ring condensation	22, 25
1370	Aliphatic C-H stretch in CH_3	22, 25
1425	Aromatic skeletal vibrations combined with C-H in -plane deform.	22, 25, 31
1460	C-H Deformations; asym. in $-CH_3$ and $-CH_2-$	22, 25, 31
1470	C-H Deformations; asym. in $-CH_3$ and $-CH_2-$	22, 25, 31
1505-1510	Aromatic skeletal vibrations aromatic C=C stretching	30, 32, 33
1596-1600	Aromatic skeletal vibrations plus C=O	30, 32
1655-1675	C=O Stretching in conjugated para-substituted aryl ketones	32, 33
1730	C=O Stretching in conjugated ketones; carbonyls and in ester groups	32, 33

three, six, and nine consecutive months of exposure in order to reveal the gradual changes of absorbency bands of reactive groups on wood surface with weathering. FTIR spectra are strongly influenced by the conditions of the sample and also by the size of the particle. Therefore, these variables must be controlled to obtain reproducible results.[30] A fine emery paper was used carefully to remove the film layer before collecting the IR-spectral samples. Sample blocks were collected from the three points (1 cm^2, at the distance of 3 cm from the sides) of the representative specimens of each group after weathering periods. Each block was inserted on a microtome (Histoslide 2000 sliding microtome, Reichert-Jung) and cut to 40 mμ thickness from the face by cutting four times (10 μm each). These specimens obtained were than finely ground in a mortar to a powdery state. Disks, 4.7 mm in diameter, were prepared from 0.005 g of wood powder and 0.5 g of potassium bromide (KBr) by compressing at 10 kg/cm^2 for one minute using a manual hydraulic pressing machine. IR spectra were obtained by using JASCO FT/IR-7000 Fourier transform infrared spectrometer.

RESULTS AND DISCUSSION

Climatic data recorded at the test site during exposure periods in summer and autumn are given in *Table* 4. The test site, which has the normal seasonal changes of a mild weathering environment with a dominantly high RH, is expected to yield realistic performance data for the tested coating systems. Observed seasons had normal levels of daily temperature and high levels of relative humidity accompanied by more sunlight and rainfall.[34]

Weight Gain

Weight gain levels of the impregnated panels are given in *Table* 5. Because of low permeability of chestnut,[35-37] chemicals were retained at one-third to one-tenth less than in Scots pine.

IR Spectral Analysis

Scots Pine: IR spectra of treated and untreated wood before and after outdoor exposure are given in *Figures* 1-4. Untreated Scots pine had undergone considerable changes at 1505 and 1596 cm^{-1} at the end of six and following three months' outdoor exposure: these two bands are assigned to C=C stretch vibration of benzene ring present in lignin (*Figure* 1, *Table* 3). The main peak converted into two very sharp peaks is shown in *Figures* 1c and 1d. Other major changes occurred at 1230-1245 cm^{-1} due to C-O stretching vibration in lignin and carbohydrates, 1330 cm^{-1} due to ring condensation, 1370 cm^{-1} due to aliphatic C–H stretch in CH_3, 1425 cm^{-1} due to aromatic skeletal vibrations combined with C–H plane deformations at 1460 cm^{-1}, and 1650-1740 cm^{-1} due to characteristic absorption of carbonyl stretching vibration of non-conjugated and conjugated esters and carboxylic acids (*Figures* 1b, 1c and 1d, and *Table* 3). Changes were developed along with weathering that evidently

Table 4—Climatic Data of the Test Site During Outdoor Exposure of the Wood Panels

Seasons	Months	Temperature (°C ± SD[a])	RH (% ± SD)	Rainfall (kg/m^2 ± SD)	Wind (m/sec)	Cloudiness (total days/month)
Summer	June-1996	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	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	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	5.6 ± 2.9	69.3 ± 10.4	4.7 ± 2.4	0.72	11

SD: Standard deviation.

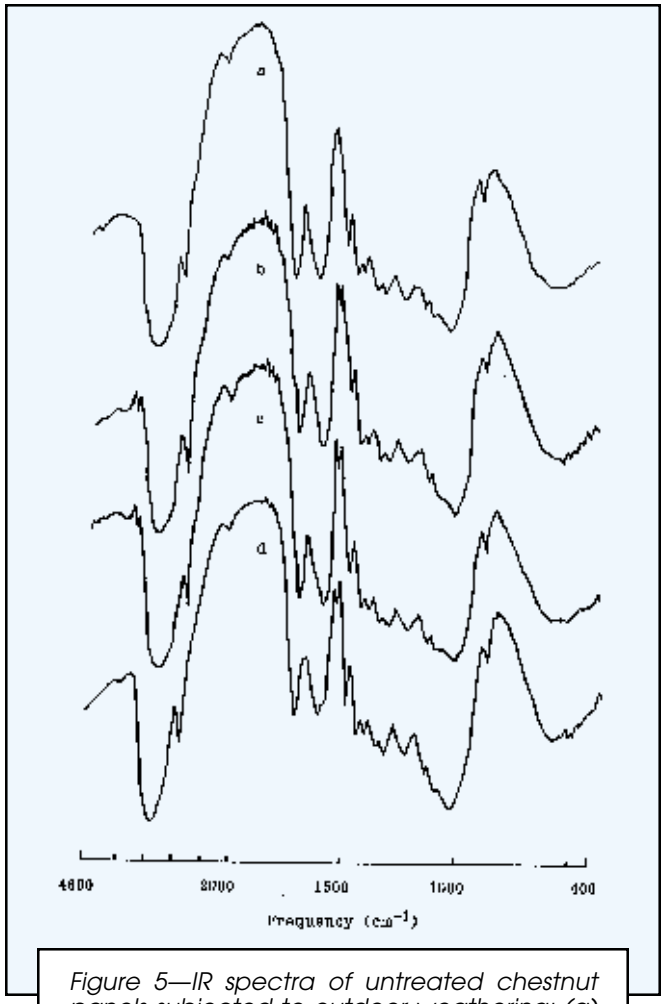

Figure 5—IR spectra of untreated chestnut panels subjected to outdoor weathering: (a) before weathering; (b) after three months of exposure; (c) after six months of exposure; and (d) after nine months of exposure.

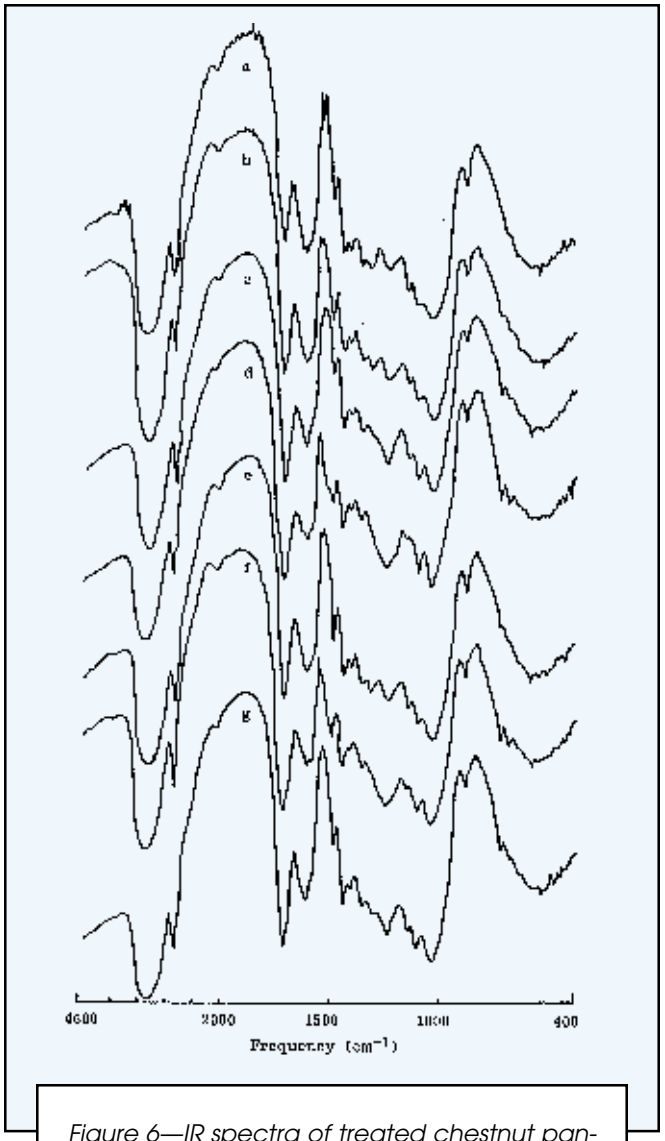

Figure 6—IR spectra of treated chestnut panels subjected to outdoor weathering for three months: (a) non-impregnated after three months of exposure; (b) CCB-treated polyurethane varnish coated; (c) CCB-treated synthetic varnish coated; (d) polyurethane varnish coated only; (e) synthetic varnish coated only; (f) WR impregnated with polyurethane varnish; and (g) WR impregnated with synthetic varnish.

reflected progressive degradation of untreated wood surface.

CCB-impregnated and polyurethane varnish-coated Scots pine boards also showed remarkable changes in lignin after weathering, but changes followed a distinctly different pattern than untreated wood (compare the related spectra (*Figures* 2b and 3b)). Three months' exposure caused a sharp decrease in peak intensity at 1505 cm^{-1} that continued for the following three months. However, no additional development occurred after nine months (*Figure* 4b). Unlike the untreated wood, no peak appeared at 1230 cm^{-1}, a band assigned to the C–C plus C–O plus C=O stretching (*Table* 3). Evans et al.[31] stated that increased absorption near 1590 cm^{-1} and reduction in intensity of the 1506 and 1263 cm^{-1} bands of non-weathered chromium trioxide treated wood are due to chemical modification of lignin. Later, Pandey et al.[38] reported the occurrence of significant changes in bands at 1740, 1660, 1596, 1506, 1464, and 1245 cm^{-1} due to chromium trioxide treatment of wood surface without exposure to weathering. They also concluded that the reduced intensity of aromatic C=C vibration at 1506 cm^{-1} and C–O vibration at 1245 cm^{-1} after chromium treatment are the evidence for modification of lignin. Additionally, it has been postulated previously that complexes formed by hexavalent chromium with the phenolic lignin units of wood are responsible for weather resistance of chromium trioxide treated wood surfaces.[39] Consequently, the changes in vibrations of bands assigned to lignin of the CCB-impregnated varnish-coated wood surface can mostly be attributed to the chemical interactions between chromium ion in CCB and lignin on wood surface apart from weathering effects within a short exposure period. In addition to the above consequences cited in literature, three reasons for this interpretation are:

(1) CCB presents a high final hexavalent chromium and can make stable complexes with wood lignin;[40]

(2) Observed changes for the CCB-impregnated surfaces appeared stable after nine months of exposure (*Figures* 2b, 3b, and 4b); and

(3) Color changes were significantly limited for the CCB-impregnated and clear varnish-coated surfaces of the same wood species.[17]

On the other hand, even at a lesser extent, change encountered was still remarkable at 1505 cm^{-1} for the CCB-impregnated and synthetic varnish coated panels (*Figures* 2c, 3c, and 4c). Other changes were milder than in untreated wood and greatly stabilized after nine months of exposure. Therefore, chemical changes in lignin and/or in assumed lignin-chromium complex appeared to depend also on the intrinsic properties of coating materials itself, its absorbency and distribution capacity of sunlight in particular. Because, IR spectra obtained from the polyurethane varnish coated panels and, more remarkably, polyurethane coating of WR-impregnated panels showed that lignin had undergone severe changes steadily in obtained vibrations (*Figures* 2d and 2f, 3d and 3f). The main peak had two shoulders to the right after three months' exposure, which developed with time. In addition, a peak at 1270 cm^{-1} assigned to C=O stretch (*Table* 3) disappeared after weathering. Other changes were observed at 1230, 1370, 1460, and 1650 cm^{-1} similar to untreated wood. Realization of relatively lesser changes in band vibrations (*Figures* 2e and 2g, 3e and 3g, and 4e and 4g) and surface color[17] for both CCB-impregnated and non-impregnated wood coated with synthetic varnish indicated the compatibility of this varnish with CCB impregnation and revealed the varying effects of outdoor weathering on different varnish types. As a result, polyurethane was found to require additional UV absorber or inhibitor for outdoor use.

In addition, the apparent difference of stretching vibrations of the bonds obtained from coatings alone and coatings over WR-treated wood may not totally reflect the changes in lignin (*Figures* 2d-2g, 3d-3g, and 4d-4g), because powders of varnish-impregnated wood as WR-treatment sampled beneath the film layers also contain varnish particles.[41-43] Therefore, similar atomic groups in organic structures of varnish components might interfere with or accompany bond stretching at similar bands.[43-45]

In the present case, chemical modification of lignin with the chromium in CCB seemed to be the main reason for the obtained color stability of CCB-impregnated wood surface coated with clear varnishes,[17] referring to the vibration change of the bond stretches assigned to lignin and stabilization of these changes as weathering progressed (*Figures* 1-4). Evidence indicated a longer time of exposure is necessary to clarify the CCB's role in weathering. Other weathering properties, such as surface hardness, glossiness, film-adhesion, and service life should also be considered for a combination treatment system of wood with CCB impregnation-clear varnish coating.

Chestnut: Untreated chestnut wood underwent some changes at 1370, 1450-1460, 1470, 1505, 1630, 1650, 1660,

Table 5—Weight Gain of Impregnated Panels

Chemical	Wood Species	Weight Gain (%±SD)
CCB	Scots pine	27.1 ± 2.5
	Chestnut	3.3 ± 0.01
Polyurethane-WR	Scots pine	20.8 ± 5.5
	Chestnut	6.2 ± 4.3
Synthetic-WR	Scots pine	33.5 ± 12.3
	Chestnut	3.8 ± 1.2

Weight gain levels of the panels due to varnish coating were 75 g/m^2 and 100 g/m^2 for the primer-and topcoating, respectively, of the same type of the varnishes. Primer was only applied over the untreated and CCB-impregnated panels.

For abbrevations refer to previous tables.

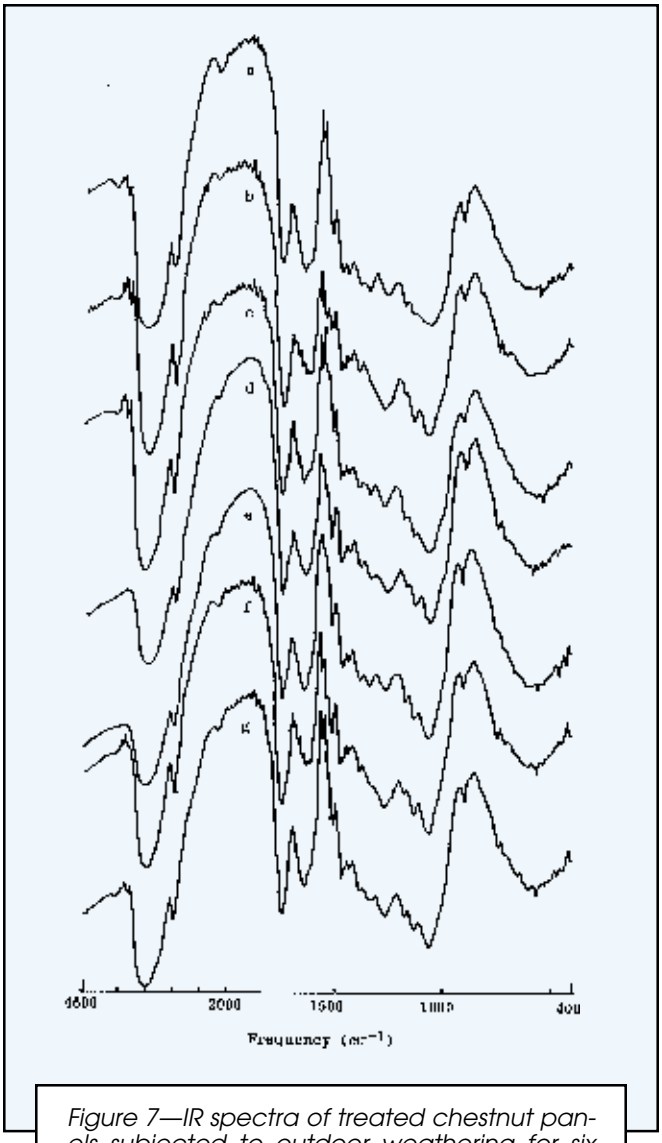

Figure 7—IR spectra of treated chestnut panels subjected to outdoor weathering for six months; (a) non-impregnated after six months of exposure; (b) CCB-treated polyurethane varnish coated, (c) CCB-treated synthetic varnish-coated; (d) polyurethane varnish coated only; (e) synthetic varnish coated only; (f) WR impregnated with polyurethane varnish; and (g) WR impregnated with synthetic varnish.

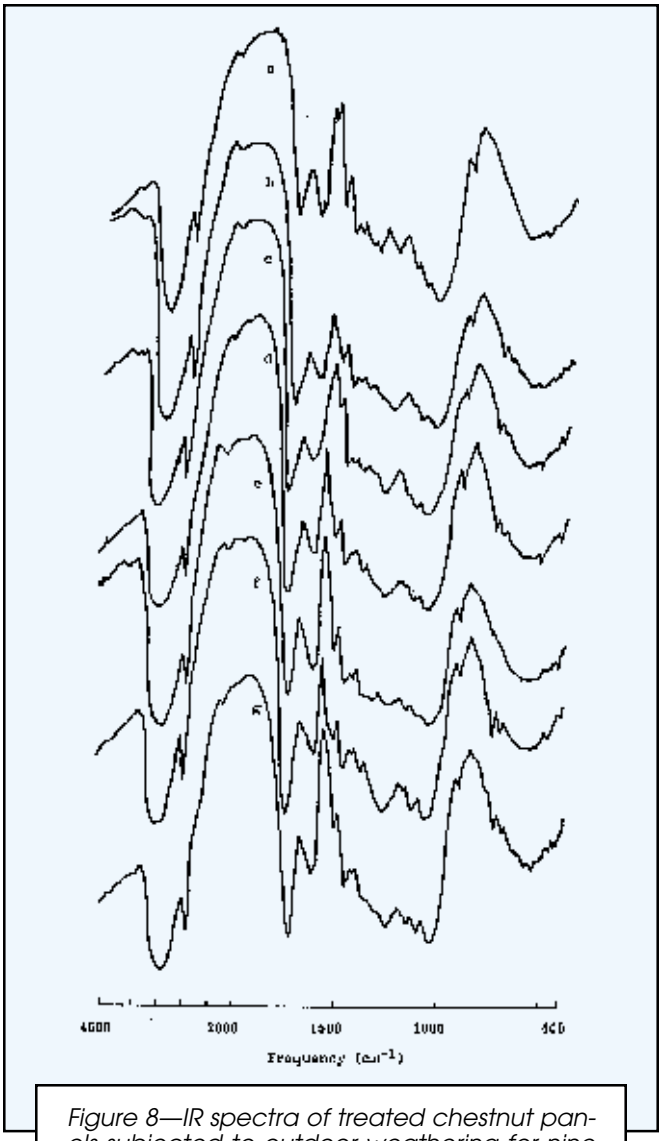

Figure 8—IR spectra of treated chestnut panels subjected to outdoor weathering for nine months: (a) non-impregnated after nine months of exposure; (b) CCB-treated polyurethane varnish coated; (c) CCB-treated synthetic varnish coated; (d) polyurethane varnish coated only; (e) synthetic varnish coated only; (f) WR impregnated with polyurethane varnish; and (g) WR impregnated with synthetic varnish.

and 1670 cm^{-1} (*Figure* 5). Two small peaks at the top of the main peak at 1505 cm^{-1} became bigger and the band got narrower as weathering progressed (*Figures* 5b and 5c). Horn et al.[46] stated that the most obvious reason for the variation in the weathering effects on different species is the difference in density in addition to other differences in chemical compositions, such as extractives, etc. A more dense structure would make it more difficult for the penetration of both light and water.[47] The effect of the high density of chestnut on the observed vibration changes was not definite for the first six months of weathering when compared to Scots pine. Hydrolyzable high tannin content of chestnut[48] is also likely to affect coating performance.[49]

Considerable changes also occurred at the observed peaks between 1655-1675 cm^{-1} which are likely to be assigned to C=O stretch in conjugated para-substituted aryl ketones (*Table* 3). Lignin seemed stable over CCB-impregnated and polyurethane varnish coated chestnut panels for the first three months of exposure, but remarkable changes were observed following weathering, particularly at 1505 and 1655-1675 cm^{-1} peaks (*Figures* 6b and 7b). Similar changes, but to lesser extents, were recorded for a CCB-synthetic varnish combination system after six months of exposure, but differences of the progressive changes between three and six months of exposure were much more prominent than that of Scots pine (*Figures* 6c and 7c).

Chestnut wood impregnated with CCB and coated with either varnishes differed with Scots pine in stability of lignin at the end of the first three months of exposure with characteristically slow, progressive changes at the initial exposure periods. However, observed changes were greatly stabilized after nine months of exposure (*Figures* 8b and 8c). Higher density of chestnut wood may have played a role in that difference probably by letting a lesser amount of the sunlight diffuse[47] to the CCB deposited sites on the surface to affect wood constituents, though untreated wood underwent steady surface degradation (*Figure* 5). If that were the case, assumed reactions between chromium and lignin might partly be time dependent for denser wood species to be activated by catalytic photoactivition of sunlight for chromium as stated earlier.[50,51] Nonetheless, 10 times lower level of color changes of the CCB-polyurethane combination compared to its single coating[17] clearly indicated that the referred changes in band vibrations after six months of exposure (*Figures* 7b and c) were mostly due to lignin modification.

Similar to Scots pine, synthetic varnish alone caused minor changes in band vibrations to lignin when applied over untreated chestnut panels (*Figures* 6e, 7e, and 8e), which proves the conclusion on the varying influence of sunlight on different varnish types. Only C=O stretch decreased in intensity after three months of exposure: detected at 1270 cm^{-1}, although some other little differences also were observed in band vibrations relative to untreated wood. When varnishes were impregnated into wood as WR, considerable changes in the vibrations of band stretches were obtained (*Figures* 6f and 6g, 7f and 7g, and 8f and8g) similar to that of Scots pine. This was probably due to the aforementioned bond stretching interference of organic components[44,45] of the varnishes in the sampled area of wood. The present results, at the very least, showed that lignin is relatively more stable on a wood surface coated with synthetic varnish. In addition, CCB impregnation followed by a synthetic varnish coating appeared to cause less chemical changes in vibration frequencies in lignin on chestnut wood surface as on Scots pine, within the studied period of time, compared to polyurethane coating that appeared to require additional UV absorber or inhibitor.

CONCLUSIONS

Differences in coating performances of a polyurethane and an alkyd-based synthetic varnish were tested on

untreated and CCB- or WR solutions on varnish-impregnated Scots pine and chestnut panels. Results for nine months of outdoor exposure were evaluated in terms of chemical changes on the wood surface. Most of the changes in vibrations of bands assigned to lignin of the CCB-impregnated varnish-coated wood surface were attributed to the chemical interactions between CCB and lignin apart from weathering effect within a short exposure period. Three observations are based on this interpretation: (1) CCB presents a high final hexavalent chromium and can make stable complexes with wood lignin[40]; (2) stability of observed spectral changes for the CCB-impregnated surfaces after nine months of exposure (*Figures* 2b, 3b, and 4b); and (3) color stability of the CCB-impregnated and clear varnish-coated surfaces of both wood species.[17] Occurrence of lesser chemical changes in vibration frequencies in lignin on both wood surfaces impregnated with CCB followed by synthetic varnish coating compared to polyurethane coating suggested that those reactions were also affected by varnish type and time dependent for denser wood species. In this respect, polyurethane varnish requires additional UV inhibitor in outdoor use.

In conclusion, CCB impregnation of wood appeared to cause some chemical modification on wood surfaces to yield probably similar complexes of chromium with phenolic lignin as true for CCA and chromium trioxide. Stability of the obtained spectral changes, in addition to the reported high stability of surface color,[17] upon successive exposure periods, offers CCB-impregnation-clear coating combination as an alternative compact treatment system for wood to resist biological and weathering effects outdoors.

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