

PHOTOPROTECTION OF COPPER-AMINE-TREATED PINE

Stephane Grelier

Assistant Professor

Alain Castellan

Professor

Laboratoire de Chimie des Substances Vegetales

Institut du Pin

Université Bordeaux 1, F

33405 Talence

Cedex, France

and

D. Pascal Kamdem†

Associate Professor

Department of Forestry

Michigan State University

East Lansing, MI 48824

(Received March 1999)

ABSTRACT

Phenolic UV absorbers containing 2-[(2''-benzotriazinyl)-4'-hydroxy-5'-tert-butylphenyl]ethylisocyanate (HBTNCO) and isocyanates of monosubstituted polyethylene glycol (350) as PEGNCO, and commercial Tinuvin 1130 (T1130) and Tinuvin precursor (PT1130) were evaluated for protection of copper-amine treated maritime pine against photodiscoloration. Treated wood was irradiated with UV (ultraviolet) light from a pressure mercury lamp of 400 watts for various periods of time. The color change after irradiation was estimated by using the CIELAB system. Grafting of HBTNCO+PEGNCO to wood surfaces using microwaves provided relatively good protection against discoloration.

Keywords: *Pinus pinaster*, copper-amine, HBT, PEG, Tinuvin, CIELAB, color, antioxidant, UV absorber, UV blocker.

INTRODUCTION

The color of the wood surface is one of the first attributes to change when wood is exposed outdoors. The change of wood color is due to light, water, and microorganisms. The deleterious effect of light on wood surfaces is thought to be due mainly to the UV light component of sunlight, which acts in combination with moisture, temperature, and oxidative agents such as oxygen and/or ozone to depolymerize lignin and cellulose in wood cell walls (Hon and Feist 1992). The yellowing, browning, and/or graying of wood surfaces

exposed outdoors indicate the modification of lignin. The depolymerization of lignin and cellulose lead also to the reduction of some physical, chemical, and biological properties of wood. Hon and Chang (1984) reported that the discoloration of wood exposed to sunlight is due to the modification of the chromophores group of wood lignin, which absorb UV light in the range of 300 to 400 nm. They found that after UV light exposure, the easily degraded products from the wood surface were low molecular weight compounds rich in conjugated phenolic hydroxyl groups derived from lignin (Zhang and Gellerstedt 1994).

The absorption of UV light by lignin promotes the formation of free radicals. The free

† Member of SWST.

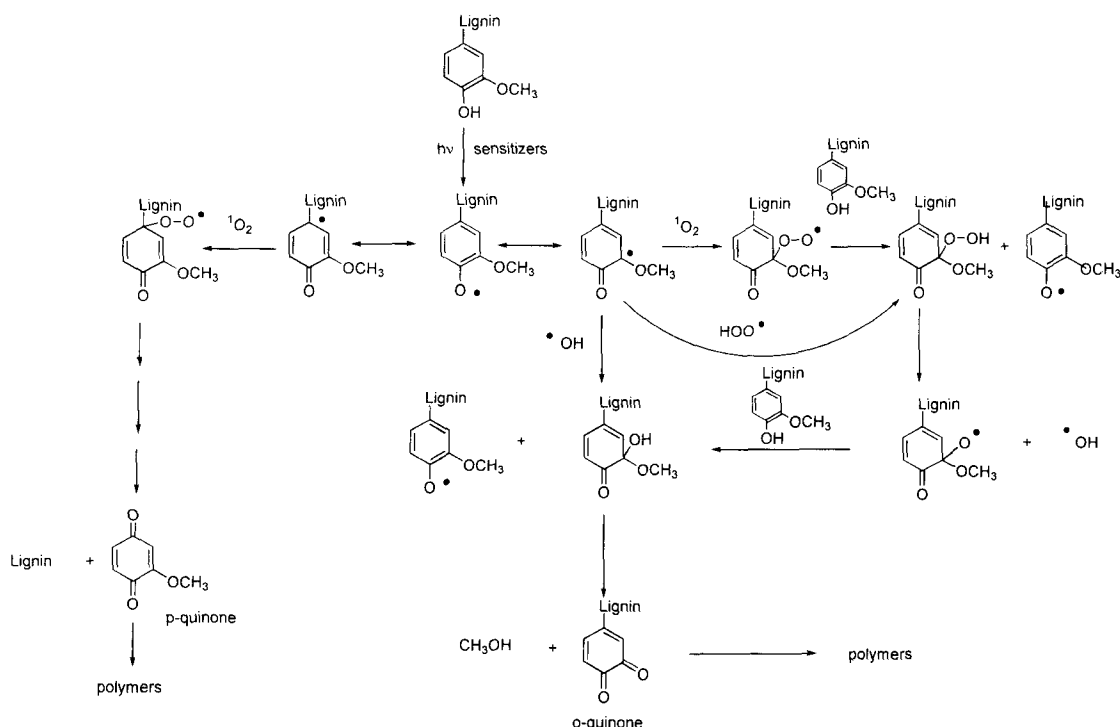


FIG. 1. Pathway of the formation of quinone.

radicals induce the depolymerization of lignin and cellulose, and the presence of oxygen facilitates the formation of oxidized radical species like hydroxyl carbonyl, carboxyl, and phenoxy radicals (Feist and Hon 1984). Leary (1968) proposed that phenoxyl radicals can lead to the formation of ortho- and/or para-quinone in both monomeric and oligomeric forms (Fig. 1). Lin and Gierer (1972) reported that the discoloration of wood and pulp is more likely due to the presence of quinone on the surface.

The protection of wood against the effect of sunlight is well documented (Feist and Hon 1984). Coatings, painting, chemical modifications, and grafting have been used to protect wood surface against discoloration (Feist 1988). Unlike coating and painting, chemical modification is a one-time treatment for the service life of wood. Etherification, acetylation, and grafting benzophenone UV light absorbers were reported as suitable methods to protect wood surfaces against photodiscolora-

tion (Rowell et al. 1993). Treatments with water-soluble salts of chromium, iron, and copper were also used to protect wood surfaces to some extent (Evans et al. 1992; Jin et al. 1991; Liu et al. 1994). It was reported that wood ion complexes formed at the wood surfaces can possibly provide resistance to wood surfaces by blocking the free phenolic groups, which are the reactive sites of photochemical reactions (Hon and Chang 1985; Ross and Feist 1991). The beneficial effects of chromium were attributed to the formation of complexes between chromium and guaiacyl units of lignin (Pizzi 1980). Antioxidants such as polyethylene glycol and UV light absorbers of hydroxyphenylbenzotriazole were tested on softwoods and reported as very effective in limiting wood surface discoloration (Hon et al. 1985). Isocyanate groups were used to graft the antioxidant on the wood surface in order to reduce the migration or the leaching of the active ingredients into the environment.

Wood exposed outdoors develops checks

TABLE 1. Color stability of treated panels and untreated control after 24-h UV irradiation.

Samples	Treatment	Cu retention, kg/m ³	Color parameters			
			ΔE^*	ΔL^*	Δa^*	Δb^*
A	Cu-EA + PT1130	1.90	6	1.0	2.5	3.0
B	Cu-EA + HBTNCO + PEGNCO	1.90	4	1.0	1.0	2.0
C	Cu-EA + T1130	1.90	6	0.5	2.5	4.0
D	Cu-EA	1.90	10	1.0	3.0	9.0
A1	PT1130	NA	13	-5.0	1.0	12.0
B1	HBTNCO + PEGNCO	NA	5	-3.0	0.5	2.0
C1	T1130	NA	13	-6.0	2.0	10.0
D1	Untreated control	NA	15	-8.0	3.0	12.0

and cracks, and this facilitates the colonization of wood by fungi and insects. Waterborne preservatives including chromated copper arsenic (CCA), copper-azole, ammoniacal copper arsenate (ACZA), and amine/ammoniacal copper quat are commercially used to treat wood at a specific retention and penetration to extend the service life of wood. The chromium in the CCA formulation contributes to the stabilization of wood surface against UV light degradation (Feist and Hon 1984). Jin et al. (1991) investigated the photodegradation of CCA- and ACQ-treated samples after 1600 h artificial weathering. They found that ACQ- and CCA-treatment retarded the progressive photo-oxidation of lignin compared to photo-oxidation in untreated samples. The same observation was reported by Liu et al. (1994).

Several emerging wood preservatives contain copper-amine (AWPA 1998). One of the potential problems of copper-amine-treated wood is color stability. The surface color of copper-amine-treated wood changes from blue-green to gray-brown after exposure to sunlight depending on the copper retention and the wood species. Black and Mraz (1974) observed and reported a significant color change on CCA-treated pine, although it was limited to just a few micrometers depth. The mechanism by which the color changes after sunlight exposure is unclear. Such information may lead to the formulation of wood preservatives with ingredients for protection against both biological and sunlight deterioration of wood. In the textile industry, commercial an-

tioxidant and UV light absorbers are commonly used to protect against color changes.

This work examined the ability of commercial antioxidants and UV light absorbers to stabilize the color of copper-amine (Cu-EA)-treated wood exposed to UV light in a laboratory setting using a CIE (Commission Internationale de l'Eclairage) system to monitor the color.

MATERIALS AND METHODS

Wood treatment

Defect-free 5- by 10- by 180-cm-long (2- by 4-in. by 6-ft) kiln-dried boards of maritime pine (*Pinus pinaster*) sapwood obtained from a sawmill located in southwestern France were used in this study. Specimens measuring 10 mm (tangential) by 20 mm (radial) by 50 mm (longitudinal) were cut from these boards and stored in the laboratory at ambient temperature.

A stock solution of Cu-EA was made by dissolving one mole of copper carbonate in four moles of mono-ethanolamine (EA). Distilled water was used to prepare the treating solution containing 1% elemental copper.

Wood specimens were vacuum-treated for 60 min in a dessicator. The copper retention of the treated wood and in the treating solution was analyzed using atomic absorption spectroscopy (AAS) following the AWPA A11-93 protocol (AWPA 1998). Table 1 contains the retention values. Cu-EA samples were stored

in the laboratory at room temperature until further testing.

Tinuvin 1130 (T1130), Tinuvin 1130 precursor (PT1130) both from Ciba-Geigy, 2-[(2'-benzotriazinyl)-4'-hydroxy-5'-tert-butylphenyl]ethylisocyanate (HBTNCO), and isocyanate of monosubstituted polyethylene glycol 350 as PEGNCO (Grelier et al. 1997) were used in this study. About 1% of each HBTNCO and PEGNCO, 2% of each T1130 and PT1130 were dissolved in acetone and sprayed on Cu-EA-treated or untreated samples. Before treatment the wood samples were dried in a microwave oven at 200 w for 2 min, and after treatment sprayed samples were microwaved at 200 w for 3 min to accelerate the reaction of isocyanate. Untreated samples were microwaved at the same condition to assess the effect of the microwave treatment. The treatment conditions are listed in Table 1.

UV light irradiation

A merry-go-round system equipped with a 400-w medium pressure mercury lamp surrounded by a borosilicate glass filter that eliminates wavelengths shorter than 300 nm was used to irradiate the samples (Fornier de Violet et al. 1989). Exposure times ranged from 0.5 to 24 h. A minimum of 5 replicate boards was used per treatment. Samples were exposed to UV light directly at a distance of 20 cm with an angle of 90°. The temperature was kept constant at $30 \pm 3^\circ\text{C}$. The relative humidity was kept at 75%, and no liquid water was sprayed on samples during the irradiation. After each irradiation period, the colors of the sample were measured.

Color measurement

The surface color of wood was determined according to ISO 2470 Standard using an Elrepho model 2000 reflectometer from Data-color. The CIELAB system is characterized by three parameters, L^* , a^* and b^* (Fig. 2). L^* axis represents the lightness, a^* and b^* are the chromaticity coordinates. In the CIELAB coordinates, $+a^*$ is for the red, $-a^*$ for green,

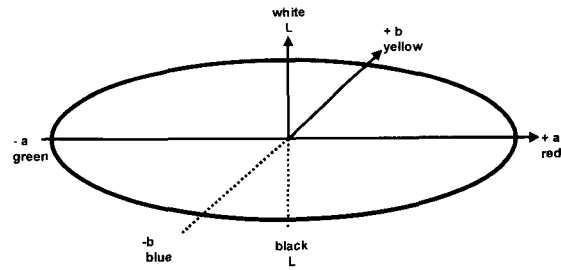


FIG. 2. Representation of CIELAB color system.

$+b^*$ for yellow, $-b^*$ for blue, and L^* varies from 100 (white) to zero (black). L^* , a^* and b^* color coordinates of each sample before and after exposure to UV light irradiation was calculated based on a D65 light source as established by the CIE 1976 (Billmeyer and Saltzman 1981). These values were used to calculate the color change ΔE^* as a function of the UV-irradiation period according to Eqs. (1), (2), (3), and (4).

$$\Delta L^* = L_f^* - L_i^* \quad (1)$$

$$\Delta a^* = a_f^* - a_i^* \quad (2)$$

$$\Delta b^* = b_f^* - b_i^* \quad (3)$$

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (4)$$

Where, ΔL^* , Δa^* , and Δb^* are the change between the initial (i) and the final (f) values. L^* , a^* and b^* contribute to the color change ΔE^* . A low ΔE^* corresponds to a low color change or a stable color. No attempt was made to measure the mass loss during the irradiation.

RESULTS AND DISCUSSION

The color changes (ΔE^*) of untreated and treated samples versus the irradiation time are represented in Fig. 3. The untreated maritime pine sample used as a control is labeled D1. Figure 3 clearly shows that the color change on the surface of wood after UV light irradiation is fast during the first four to five hours, and thereafter the rate of change diminishes.

The most effective method of stabilizing wood color involved treatment with Cu-

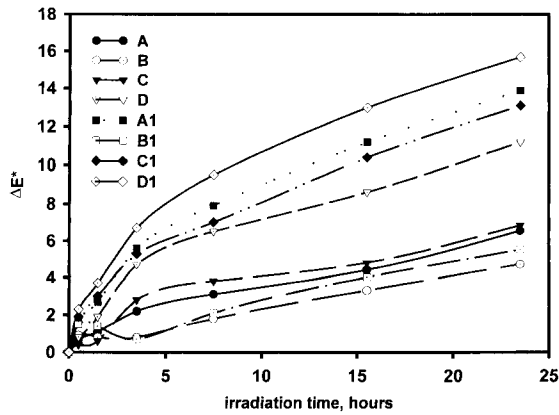


FIG. 3. Color stability (ΔE^*) versus the duration of UV light irradiation of sample treated with Cu-MEA+PT1130 (A); Cu-MEA+HBTNCO+PRGNCO (B); Cu-MEA+T1130 (C); Cu-MEA (D); PT1130 (A1); HBTNCO+PRGNCO (B1); T1130 (C1); untreated control (D1).

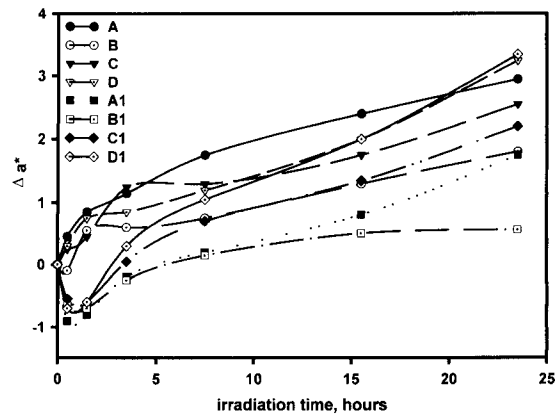


FIG. 5. Red-green stability (Δa^*) versus the duration of UV light irradiation of sample treated with Cu-MEA+PT1130 (A); Cu-MEA+HBTNCO+PRGNCO (B); Cu-MEA+T1130 (C); Cu-MEA (D); PT1130 (A1); HBTNCO+PRGNCO (B1); T1130 (C1); untreated control (D1).

EA, followed by a second treatment with HBTNCO+PEGNCO and then, microwaving. The microwaving accelerates the grafting of HBT and PEG via urethane bond after the reaction of isocyanate and hydroxyl groups present on the wood surface (Grelier et al. 1997). The color change of microwaved and unmicrowaved untreated reference sample was not significant, suggesting

that the effect of microwaving was negligible on reference samples.

Treatment with HBTNCO+PEGNCO stabilized wood color more effectively than untreated control or other treatments, but less than for the Cu-EA and grafting treatment. This suggests a positive contribution of Cu-EA to wood color stability in accord with previous studies (Jin et al. 1991; Liu et al. 1994).

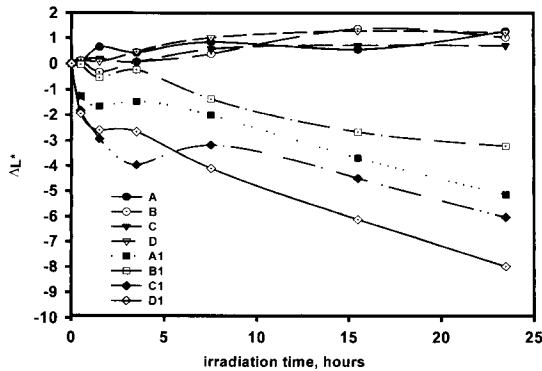


FIG. 4. Lightness stability (ΔL^*) versus the duration of UV light irradiation of sample treated with Cu-MEA+PT1130 (A); Cu-MEA+HBTNCO+PRGNCO (B); Cu-MEA+T1130 (C); Cu-MEA (D); PT1130 (A1); HBTNCO+PRGNCO (B1); T1130 (C1); untreated control (D1).

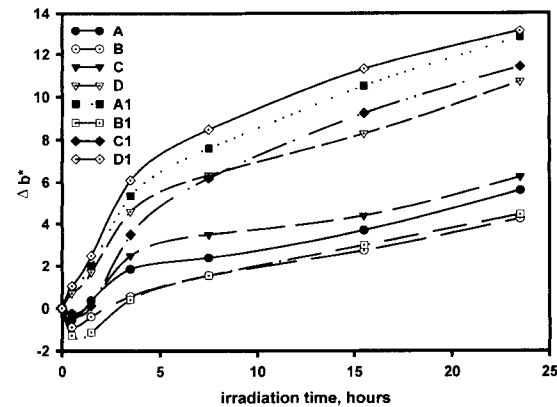


FIG. 6. Yellow-blue stability (Δb^*) versus the duration of UV light irradiation of sample treated with Cu-MEA+PT1130 (A); Cu-MEA+HBTNCO+PRGNCO (B); Cu-MEA+T1130 (C); Cu-MEA (D); PT1130 (A1); HBTNCO+PRGNCO (B1); T1130 (C1); untreated control (D1).

ACQ-treatment was reported to slow wood photodegradation via inhibiting the formation of carbonyls and delignification during weathering (Liu et al. 1994).

The value of ΔE^* for the untreated control, which was +15.7 as measured by CIELAB system, is a clear indication of color change after 24-h exposure. This color change can be separated in contribution from ΔL^* of -7.98, Δa^* of +3.35, and Δb^* of +13.1 (Table 1). The negative ΔL^* values probably occur because the wood surface becomes rougher and darker during UV light irradiation. Depolymerization of the lignin on the exposed surface may also render the surface darker (Hon 1981). The increase of the chromaticity coordinates Δa^* by +3.35 and Δb^* by +13.1 may be explained by the modification of some chromophoric groups of lignin. The depletion of the chromophore groups is related to the formation of species absorbing in the visible region of the spectrum as proposed in Fig. 1. The recovery of chromophoric groups capable of absorbing UV light in the region ranging from 300 to 550 nm was reported for UV light-irradiated *Abies*. The color change was attributed to the carbonyl group of conjugated ketones, aldehydes, and quinones resulting from the modification of the lignin and other related compounds (Castellan and Davidson 1994).

After 24-h UV light irradiation, Cu-EA-treated samples (labeled D) had a much lower ΔE^* (+10.2) than untreated samples (+15.7, D1). The contributions of the chromaticity coordinates Δa^* and Δb^* were similar to that of untreated control. The values of ΔL^* for Cu-EA-treated samples was lower than the values obtained for untreated samples. Cu-EA-treatment improves the stabilization of wood color in the visible region, likely by reducing the lignin degradation resulting from UV light irradiation. The stabilization of lignin by chromium or iron was reported to occur through the formation of complexes (Williams and Feist 1985; Evans et al. 1992). Similar complexes may be formed with copper.

Treatment of the untreated control and Cu-

EA-treated samples with PT1130 stabilized wood color after 24-h UV light irradiation, but the value of ΔE^* suggests better color stability for Cu-EA pretreated samples. The low value of ΔL^* confirms the contribution of copper treatment to the color stability.

The pretreatment with Cu-EA followed by a spray-treatment with HBTNCO+PEGNCO (B) provided the best color stability. The ΔL^* of all samples pretreated with Cu-EA (A, B, C, and D) was almost similar, but lower than the values obtained for untreated control or samples not pretreated with Cu-EA (Table 1). These findings suggest that copper forms some complexes with wood components capable of reducing the degradation of the wood surface that contributes to a relatively important modification of the roughness and/or the lightness of the wood surface. This is in agreement with the literature (Hon and Chang 1985; Evans et al. 1992) stating that inorganic ions, namely ferric and chromium ions, can prevent the formation of peroxides, which promote the photodegradation of wood surfaces.

The lowest values of Δa^* were obtained on wood treated with the UV light stabilizers HBTNCO+PEGNCO and PT 1130. The highest value was measured on the untreated control and on Cu-EA-treated samples. The same observations were made for Δb^* . The treatment of samples with T1130 or PT1130 resulted in samples with negative ΔL^* , high Δb^* , and relatively stable Δa^* . The action of the Tinuvin T1130, a commercial product, is almost similar to the effect of the precursor of Tinuvin PT1130 on Δa^* . The actions of these two additives are different from that of the polyethylene glycol chain chemically bonded to the hydroxybenzotriazole moiety by an ester function and grafted on the wood with isocyanate.

CONCLUSIONS

UV light absorbers were used in conjunction with a copper-amine preservative to treat pine in order to evaluate their efficacy as wood color photostabilizers. Treatment of wood by

a copper-amine solution followed by the grafting of a mixture of PEG and HBT using urethane bond from the isocyanate was found very effective in stabilizing wood color. Copper-amine treatment also reduced discoloration, possibly because it retarded the depolymerization of lignin at wood surfaces, which limits the variation of ΔL^* . Treatment with HBTNCO+PEGNCO increased color stability by limiting the variation of Δa^* and Δb^* .

REFERENCES

- AMERICAN WOOD PRESERVERS' ASSOCIATION (AWPA). 1998. Book of standards. Granbury, TX.
- BILLMEYER, F. W. J., AND M. SALTZMAN. 1981. Principles of colour technology. John Wiley and Sons, New York, NY. 240 pp.
- BLACK, J. M., AND E. A. MRAZ. 1974. Inorganic surface treatments for weather-resistant natural finishes. USDA, For. Serv. FPL Res. Pap. 232, Madison, WI.
- CASTELLAN, A., AND R. S. DAVIDSON. 1994. Steady-state and fluorescence emission from *abies* wood. J. Photochem. Photobiol. A: Chem. 78:275-279.
- EVANS, P. D., A. J. MICHELL, AND K. J. SCHMALZL. 1992. Studies of the degradation and protection of wood surfaces. Wood Sci. Technol. 26(2):151-163.
- FEIST, W. C. 1988. Weathering performance of finished southern pine plywood siding. Forest Prod. J. 38(3):22-28.
- , AND D. N. S. HON. 1984. Chemistry of weathering and protection. Pages 401-451 in R. M. Rowell, ed. The chemistry of solid wood. Advances in Chemistry Series, No. 207. American Chemical Society, Washington, DC.
- FORNIER DE VIOLET, P., A. NOURMAMODE, N. COLOMBO, AND A. CASTELLAN. 1989. Study of brightness reversion of bleached chemithermomechanical pulp by solid state electronic spectroscopy. Cell. Chem. Technol. 23:535-544.
- GRELIER, S., A. CASTELLAN, S. DESROUSSEAU, A. NOURMAMODE, AND L. PODGORSKI. 1997. Attempt to protect wood color against UV/visible light by using antioxidants bearing isocyanate groups and grafted to the material with microwave. Holzforchung 51(6):511-518.
- HON, D. N. S. 1981. Photodegradation of lignocellulosic materials. In N. Grassie, ed. Developments in polymer degradation. Chapter 8. Applied Science Publication, London, UK.
- , AND S. T. CHANG. 1984. Surface degradation of wood by UV light. J. Polym. Sci.: Polym. Chem. Ed. 22:2227-2241.
- , AND S. T. CHANG. 1985. Photoprotection of wood surfaces by wood-ion complexes. Wood Fiber Sci. 17(1):92-100.
- , AND W. C. FEIST. 1992. Hydroperoxidation in photoirradiated wood surfaces. Wood Fiber Sci. 24(4):448-455.
- , S. T. CHANG, AND W. C. FEIST. 1985. Protection of wood surfaces against photooxidation. J. Appl. Polym. Sci. 30:1429-1448.
- JIN, L., K. ARCHER, AND A. PRESTON. 1991. Surface characteristics of wood treated with various AACs, ACQ, and CCA formulations after weathering. The International Research Group on Wood Preservation Document No IRG/WP/2369, 10 pp.
- LEARY, G. 1968. Photochemical production of quinoid structures in wood. Nature 217:672-673.
- LIN, S. Y., AND J. GIERER. 1972. Photodegradation of lignin. A contribution to the mechanism of chromophore formation. Sven. Papperstidn 75:257-260.
- LIU, R., J. N. R. RUDDICK, AND L. JIN. 1994. The influence of copper (II) chemicals on the weathering of treated wood, Part I. ACQ treatment of wood on weathering. The International Research Group on Wood Preservation Document No IRG/WP/30040, 9 pp.
- PIZZI, A. 1980. Wood waterproofing and lignin crosslinking by means of chromium trioxide/guaiacyl units complexes. J. Appl. Polym. Sci. 25:2547-2553.
- ROSS, A. S., AND W. C. FEIST. 1991. The effects of CCA-treated wood on the performance of surface finishes. Proc. Amer. Wood Preservers Assoc., pp. 1-15.
- ROWELL, R. M., R. S. LICHTENBERG, AND P. LARSSON. 1993. Stability of acetylated wood to environmental changes. Wood Fiber Sci. 25(4):359-364.
- WILLIAMS, R. S., AND W. C. FEIST. 1985. 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 Fiber Sci. 17(2):184-198.
- ZHANG, L., AND G. GELLERSTEDT. 1994. Reactive structures in wood and high-yield pulps. Acta Chem. Scand. 48:490-497.