

STABILIZATION OF WOOD COLOR: IS ACETYLATION BLOCKING EFFECTIVE?

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ABSTRACT

The color of acetylated wood was assessed by studying its response to ultraviolet light during a 56-day exposure. Change in color and reduction of reflectance signaled an interaction of acetylated wood with electromagnetic energy. Acetylated wood exhibited a color stabilization effect better than did unacetylated wood after the initial 28 days of irradiation. Its stabilization effect thereafter steadily diminished and discoloration started. Electron spin resonance (ESR) studies of photoirradiated acetylated wood and milled wood lignin divulged the generation of an active methyl radical and stable phenoxy radicals during irradiation, contributing to a quartet and a singlet signal. These free radicals originated from deacetylation and demethoxylation reactions to lignin. Moreover, ESR studies of the acetylated model compound, (4'-methyl-2'-methoxy phenoxy)- β -hydroxypropiovanillone, also divulged the cleavage of the β -O-4 linkage in lignin. It is concluded that these photo-induced degradative reactions led to the formation of phenoxy radicals which were the principal intermediates leading to the subsequent chromophoric group formations in acetylated wood.

Keywords: Acetylation, weathering, color, discoloration, ESR, reflectance, radical, yellow pine, lignin.

INTRODUCTION

Wood has always held a special place in our culture because of its many enchanting properties, one of which is the absorption and reflection of light, resulting in color and gloss. The color characteristics depend on the chemical components of wood that interact with light. If the interaction takes place with longer wavelengths, i.e., weaker electromagnetic energy, only photophysical phenomena but no chemical reaction or degradation will take place. If the interaction occurs with shorter wavelengths, in addition to photophysical phenomena, photochemical phenomena also take place. Wood used outdoors is exposed to solar energy, which is comprised of a small portion of the ultraviolet (UV) light starting from 294 nm and extending into the visible region. The energy falling in this region is sufficient to cleave most of the covalent bonds found in wood (Hon 1991). In the absence of alternate non-damaging pathways for the absorbed energy to

dissipate, the polymeric wood component will use the energy for chemical reactions, which ultimately lead to discoloration and loss of gloss in wood. It should be borne in mind that the natural weathering of wood also involves many other elements such as heat, oxygen, moisture, microorganisms, and air pollutants (Hon and Feist 1992, 1993; Hon 1994). These elements may also contribute to discoloration of wood. Since ultraviolet light has been singled out as the most damaging factor contributing to discoloration, in this article we shall limit our discussion to photo-induced discoloration reactions.

In order not to camouflage the natural texture and color of wood, many approaches have been developed to avoid discoloration of wood by using different clear-coating materials. Most of them do not function effectively, and some of the promising ones turned out to be too expensive to be used. In addition, many UV absorbers, quenchers, and hindered amine light stabilizers have also been used.

It has been proved that the color in wood is due mostly to a series of photochemical reactions of lignin. Many scientists have shown that the blocking of phenolic hydroxy groups in lignin in wood by etherification (Peill 1946; Singh 1966) and esterification (Lorås 1968; Leary 1968; Manchester et al. 1960) can achieve photostabilization and improve weatherability and color stabilization. One of these methods that has gained popularity recently is acetylation. Reports of dimensional stability (Kumar et al. 1991), biological resistance (Imamura and Nishimoto 1986, 1987), and improved weatherability (Feist and Rowell 1991; Plackett et al. 1992; Dunningham et al. 1992) of wood by acetylation have also been found. The first patent for acetylation of wood using acetyl chloride was granted to Suida in 1930 (Suida 1930), and the use of acetic anhydride was also developed more than 50 y ago. Despite its old chemistry, in recent years many scientists have reevaluated the acetylation methods and become convinced of acetylation's technical feasibility. The preparation of acetylated wood and fiber has reached commercial success in Japan, and commercial feasibility is also being considered in England (Sheen 1992).

The principal reaction of acetylation in wood is to substitute hydroxyl groups in the polymeric components of wood, mainly cellulose and lignin. As mentioned earlier, acetylation of wood has improved its weatherability and color stability (Leary 1968; Ek et al. 1991; Feist and Rowell 1991; Plackett et al. 1992; Dunningham et al. 1992). Dawson and Torr reported that acetylation suppressed formation of a chromophore, which absorbs at 530 nm (Dawson and Torr 1992). Nonetheless, a gradual discoloration is still observed in acetylated wood and pulp on exposure to light over long periods of time. Apparently, acetylated wood is not immune from photoreaction. In this paper, we would like to report our study on photoactivity of acetylated wood. The results may shed some light on the causes of instability of chemically modified wood and related lignocellulosic materials.

EXPERIMENTAL

Materials

Southern yellow pine (*Pinus* spp.) was used for this study. For the discoloration study, earlywood strips with a dimension of 80 mm × 10 mm × 0.125 mm were prepared with a microtome. For the ESR study, microtome sections 30 mm long, 2 mm wide, and 100 μ m were prepared. Milled wood lignin of southern yellow pine was obtained by milling wood meal in 1.3-gal Roalox porcelain mill jars and purifying according to Bjorkman's method (Bjorkman 1956). A model compound, (4'-methyl-2'-methoxy phenoxy)- β -hydroxypropiovanillone, was synthesized according to a modified method described in the literature (Adler and Marton 1961).

Acetylation

The acetylation method was based on a simplified procedure proposed by Rowell et al. (1986). Simply, the specimens, with a moisture content of 5%, were dipped in acetic anhydride for 15 min. The excess acetic anhydride was removed by draining. The treated wood was placed in a preheated (115–120 C) glass reactor equipped with a condenser and heated for a designated time. After reaction, the specimens were washed with distilled water to remove unreacted acetic anhydride and acetic acid. Acetylated woods with different weight gain were prepared. The specimens were conditioned in a desiccator for 3 days prior to the photoactivity study. Acetylated milled wood lignin and model compound were also prepared by a similar method.

Photoactivity study

For spectroscopic evaluation, wood strips were irradiated in a weatherometer (Atlas, Model 600-WR). The temperature in the irradiation chamber was about 45 C, and relative humidity was 55%. The irradiation light source was a xenon light (600 W). For the ESR study, the wood specimen was inserted into a Suprasil quartz ESR sample tube, which was then sealed under vacuum (10^{-6} mm Hg). The

tube was inserted into a Dewar flask filled with liquid nitrogen. The source of UV irradiation was a high-pressure quartz mercury-vapor lamp (ACE-Hanovia, lamp type 6531-12, 200 W) with a pyrex window where wavelengths <292 nm were cut off. ESR spectra were measured with an X-band ESR spectrometer (Varian E-12, 100 kHz field modulation). To avoid undesired secondary free radicals and obtain ESR maximum sensitivity, ESR measurements were carried out at 77 K (−196 °C) by inserting the liquid-nitrogen-filled Dewar flask into the ESR spectrometer cavity.

Evaluation

The extent of discoloration of exposed surfaces was examined by using a spectrophotometer (LabScan II, Hunter Lab.). The color of wood was subjectively measured with an illuminant D light source (D65, 6500 K) with a measuring aperture of 6 mm. A white tile was placed behind the sample to enrich the light reflectance. Reflectance spectra of exposed wood were also recorded. Illumination of the specimen was about perpendicular to the specimen plane (0 illustration), and viewing was performed at an angle of 45°. Twelve measurements were made to obtain an average value. The CIE color difference system was used.

RESULTS AND DISCUSSION

The mechanism of acetylation of wood has been established for a long time. A simplified reaction scheme is shown in Eq. 1.

After acetylation, earlywood specimens changed their color from yellow to light pale yellow, and milled wood lignin changed from gray to light yellow. This brightening effect is due to the substitution of phenolic hydroxyl groups in lignin.

Discoloration

When acetylated wood was irradiated with ultraviolet light, a change in color was observed. The change in color, as illustrated by

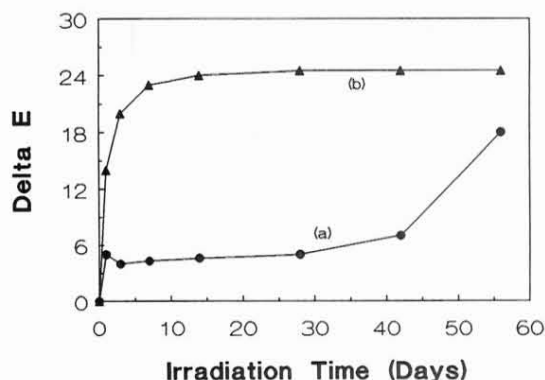
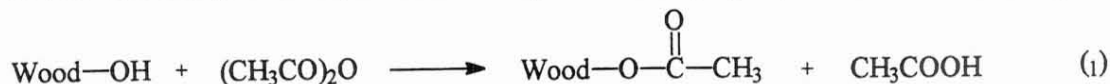


FIG. 1. Color difference of unacetylated (b) and acetylated woods (a) irradiated with ultraviolet light.

color difference (ΔE), during 56 days of irradiation is depicted in Fig. 1. After 24 hours of irradiation, the value of color difference between irradiated and unirradiated acetylated woods was 5 units. The modified color appeared to be stabilized for up to 28 days of irradiation. However, the rate of change in color accelerated thereafter. After 56 days of irradiation, the color difference value was registered as 18 units. It was a severe discoloration. For comparison, untreated wood was also irradiated under identical conditions, and a drastic change of color is also depicted in Fig. 1. Apparently, the untreated wood lost its color rapidly in the initial 7 days of irradiation. The color difference value was 23 units. The rate of color change slowed down after 7 days of irradiation, and appeared to be stabilized after 14 days. These data substantiated that acetylated wood achieves some degree of color stabilization, especially during the first 28 days of irradiation. Unfortunately, the effectiveness of color stabilization was reduced significantly after 28 days of irradiation.

Loss of reflectance

The change in color signals the change in chemical structures on the wood surface. This change can be monitored by the change in reflectance property of the wood surface (Hon



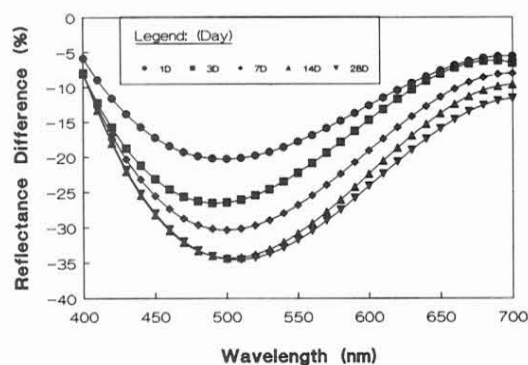


FIG. 2. Reflectance difference curves of unacetylated wood irradiated with ultraviolet light.

and Chao 1989). Put simply, the more that color absorbs the light, the less reflectance occurs. Hence, a reflectance spectrophotometer was used to study the reflectance change.

The differences in reflectance of unacetylated wood before and after irradiation are shown in Fig. 2. During 28 days of irradiation, the loss of reflectance took place significantly after 14 days of irradiation. Most of the reflectance loss was due to the change in the blue and orange regions (500–600 nm) of reflectance. The loss between 14 and 28 days of irradiation was not a significant difference. This result is in agreement with the color difference data discussed earlier.

After one day of irradiation of acetylated wood, it is interesting to notice that the irradiated wood was brighter (Fig. 3). A similar phenomenon was reported by Callow (Callow 1947; Callow and Speakman 1949). They postulated that the brightening or bleaching effect was due to the formation of acetyl peroxide during irradiation of acetylated wood. Lorås (1968) considered that the bleaching mechanism might be the possible explanation for the stabilizing effect of acetylation. Although the bleaching effect was observed, its effectiveness diminished gradually between 3 and 28 days of irradiation. After 42 days of irradiation, the brightening effect was lost and discoloration became conspicuous. Additional loss was observed when irradiation was extended to 56 days. Again most of the loss was in the region of 460–550 nm.

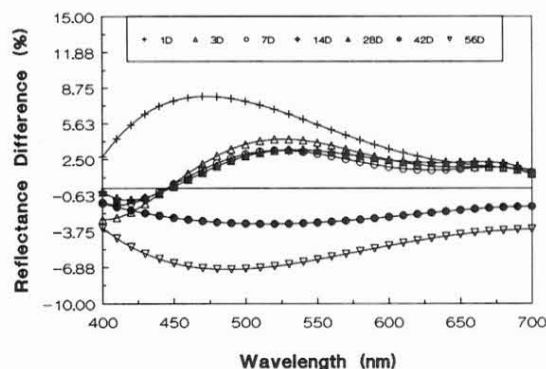


FIG. 3. Reflectance difference curves of acetylated wood irradiated with ultraviolet light.

In a comparison of acetylated and unacetylated woods, it is obvious that acetylation provided a certain degree of protection or color stabilization. Unfortunately, the stabilization is not effective after 28 days of irradiation. This phenomenon suggested the possibility of interaction between acetyl groups and light. After acetylation, lignin may continue to participate in photo-induced discoloration. Plackett et al. (1992) suggested that the loss of protection after irradiation, under accelerated weathering for 8 weeks, may be due to the loss of acetyl groups. In order to obtain information on photoactivity of acetylated wood, ESR spectroscopy was used to elucidate the intermediate species generated in photoirradiated acetylated wood.

ESR studies

Based on the color change and reflectance difference studies, the results implied that acetylation provided a temporary stabilization effect during the 28 days of irradiation. Acetylation lost its effectiveness if irradiation continued.

When acetylated wood was irradiated with the ultraviolet light for 60 min at 77 K, a multiplet spectrum with a *g* value of 2.003 was detected, as shown in Fig. 4(B). This spectrum was quite different from that of irradiated untreated wood (Fig. 4A). The diffuse multiplet signals of irradiated wood were a superposition of signals from various radicals from cellulose and lignin. Detailed studies of these radicals

have been discussed elsewhere (Hon 1991). When the irradiated acetylated wood was warmed to 273 K for 1 min and recorded again at 77 K, only a single spectrum with a line-width of 15 gauss was observed, and the outward four peaks disappeared, indicating the instability of the corresponding free radical intermediates at room temperature. The irradiation of acetylated milled wood lignin under identical conditions exhibited a strong multiplet signal (Fig. 4C), in which the prominent four peaks disappeared rapidly at room temperature and left a diffuse vestigial singlet signal with a line width of 14 gauss. Because of the similarity of ESR profiles and their decaying characteristics, we were led to conclude that identical free radical intermediates that generated the singlet and quartet signals were derived from the lignin component. The singlet signal originated from phenoxy radicals. Since the four peaks exhibited a splitting constant of 22.5 gauss, there is little doubt that it is a quartet spectrum derived from methyl radicals (Hon 1977). Apparently, they were the intermediate products of demethylation or deacetylation. Demethylation may be due to the cleavage of methoxyl groups in lignin or the cleavage of acetyl groups. Further experimental study showed that the quartet component of the signal increased as the acetyl content of the specimen increased, suggesting that demethylation of acetyl group and deacetylation are preferential reactions to the demethylation of methoxy groups. To illustrate these reactions in acetylated wood and lignin, a simplified reaction scheme is shown here (Eqs. 2-5):

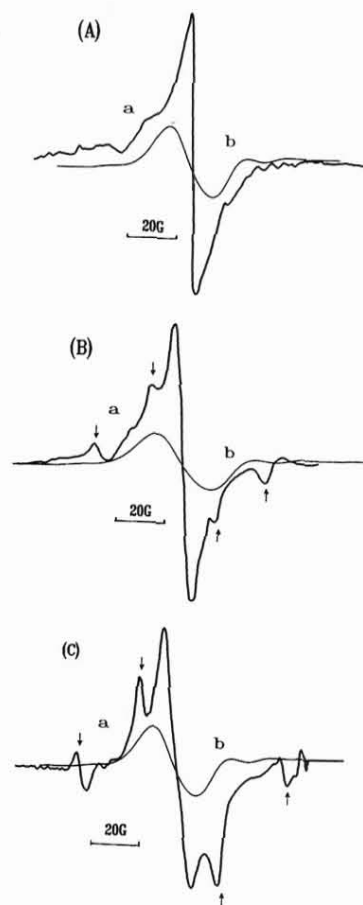
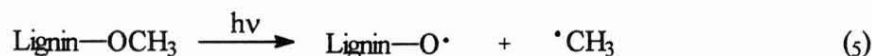
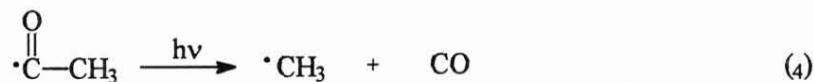
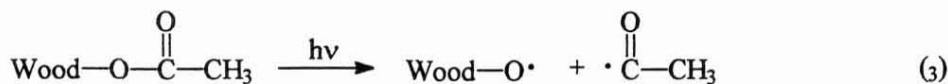
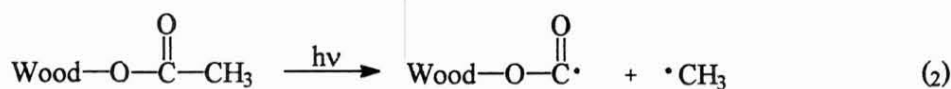
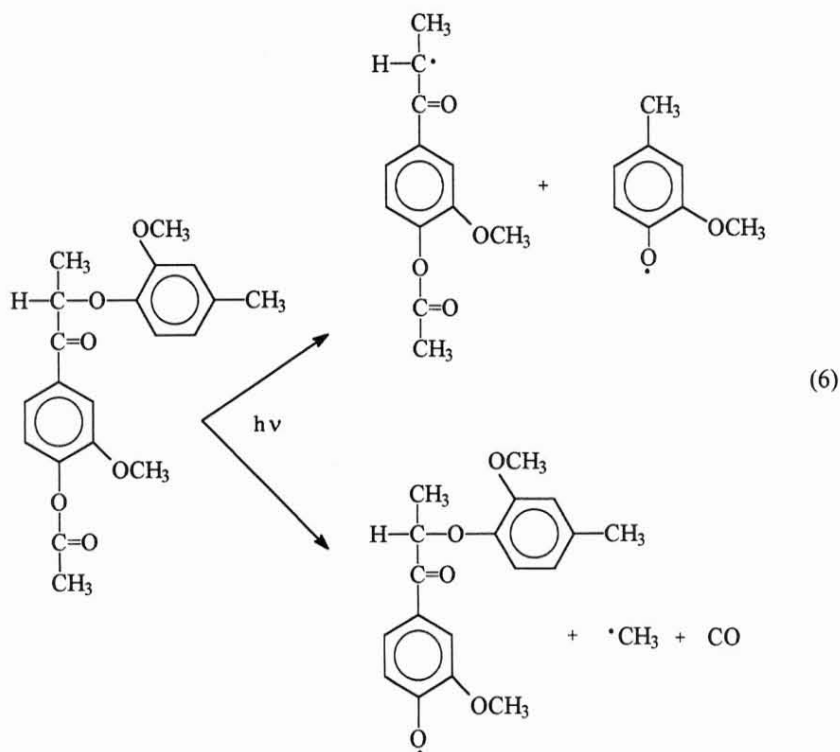


FIG. 4. ESR spectra of wood (A), acetylated wood (B), and acetylated milled wood lignin (C). The singlet signal (b) was observed after the irradiated specimen (a) was warmed to 273 K for 1 min. All spectra were recorded at 77 K. The arrow sign denotes the location of the four peaks.

Since the α -carbonyl group is an important light absorption center to promote photodegradation and discoloration of lignin (Hon 1992), the investigation of its role in acetylated wood is imperative. Accordingly, a model compound, namely (4'-methyl-2'-methoxyphenoxy)- β -hydroxypropiovanillone, and its acetylated derivative were prepared for photoirradiation and ESR evaluation. When the unacetylated model compound was irradiated at 77 K, a prominent five-line spectrum was observed as shown in Fig. 5(A). When the specimen irradiated was warmed to 298 K for 1 min and recorded again at 77 K, the five-line spectrum transformed into a singlet signal with a line-width of 15 gauss and a g-value of 2.003. Apparently, the β -O-4 aryl ether bond was cleaved to generate the five-line and the singlet signal. Interpretation of these ESR signals was discussed elsewhere (Hon 1992). When the acetylated model compound was irradiated at 77 K, a complicated multiplet spectra was observed as shown in Fig. 5(B). Careful

examination of the spectrum revealed the superposition of a five-line and a four-line signal. The former was due to the cleavage of the β -O-4 aryl ether linkage, and the latter was due to the methyl radicals originated from demethylation of acetyl groups or demethoxylation, as discussed earlier. The reaction scheme is shown in Eq. 6.

The study of changes in color and reflectance of acetylated wood showed that acetylated wood lost its color stabilization after 24 hours of irradiation. ESR studies implied that one of the reasons for the color change is the deacetylation reaction. Leary (1968) suggested that free phenolic groups in acetylated wood are regenerated over time by the cleavage of acetyl groups. The other reason is the cleavage of β -O-4 aryl ether linkage. In this reaction, a phenoxy radical is generated. It is well documented (Hon 1991) that the phenoxy radical is the major culprit that leads to the formation of chromophoric groups, especially the quinonoid structures in lignin.



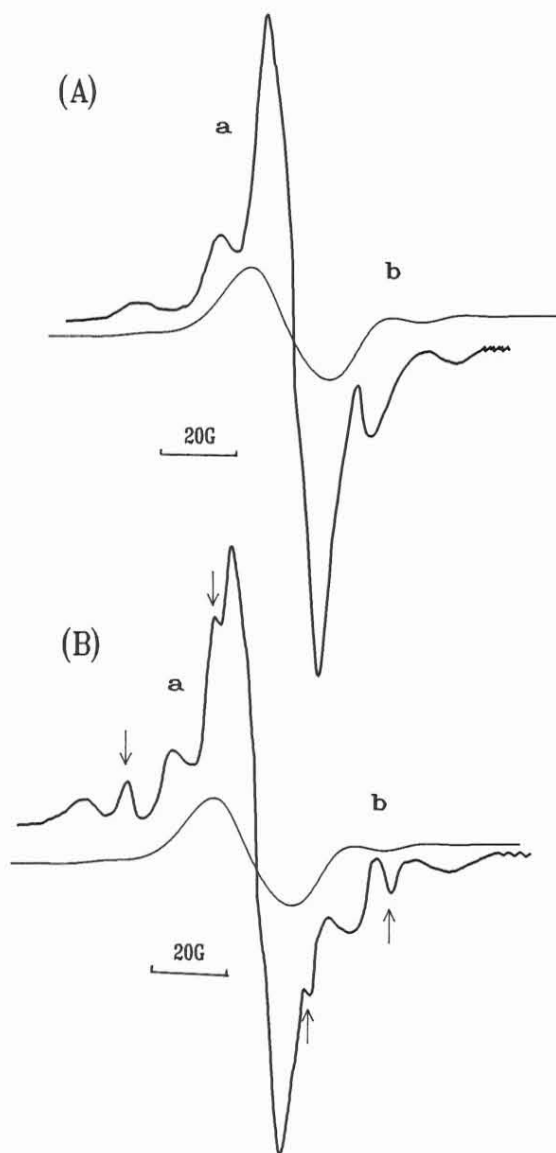


FIG. 5. ESR spectra of (4'-methyl-2'-methoxy phenoxy)- β -hydroxypropiovanillone (A) and acetylated (4'-methyl-2'-methoxy phenoxy)- β -hydroxypropiovanillone (B). The singlet signal (b) was observed after the irradiated specimen (a) was warmed to 273 K for 1 min. All spectra were recorded at 77 K. The arrow sign denotes the location of the four peaks.

CONCLUSIONS

Based on these experimental findings, the following conclusions may be drawn:

1. Acetylated wood is reactive toward light. It

changed its color and lost surface reflectance when irradiated with the ultraviolet light.

2. Acetylation was effective in providing temporary retardation of color change in southern yellow pine during 28 days of irradiation but thereafter was less effective.
3. ESR evidence suggests that deacetylation and cleavage of β -O-4 lead to regeneration of phenoxy radicals, which are the major culprits of discoloration in acetylated southern yellow pine.

REFERENCES

- ADLER, E., AND J. MARTON. 1961. Carbonyl groups in lignin. II. Catalytic hydrogenation of model compounds containing aryl carbinol, aryl carbinol ether, ethylene, and carbonyl groups. *Acta Chem. Scand.* 15:357.
- BJORKMAN, A. 1956. Studies on finely divided wood. Part I. Extraction of lignin with neutral solvents. *Sven. Papperstidn.* 59(13):477-485.
- CALLOW, H. J. 1947. Action of light upon jute. *Nature* 159:309.
- , AND J. B. SPEAKMAN. 1949. Yellowing of jute. *J. Soc. Dyers Colorists* 65:758.
- DAWSON, B., AND K. TORR. 1992. Spectroscopic and color studies on acetylated radiata pine exposed to UV and visible light. Pages 41-51 in D. V. Plackett and E. A. Dunningham, eds. *Proc. Pacific Rim Bio-Based Composites Symposium*. November 1992, Forestry Research Institute, New Zealand. FRI Bull. No. 176.
- DUNNINGHAM, E. A., D. V. PLACKETT, AND A. P. SINGH. 1992. Weathering of chemically modified wood. Natural weathering of acetylated radiata pine: Preliminary results. *Holz Roh- Werkst.* 50:429-432.
- EK, M., M. H. LENNHOLM, G. LINBLAD, AND T. IVERSEN. 1991. The light induced color reversion of groundwood pulps. A study on the mechanism of chromophore formation. 6th International Symposium on Wood and Pulp Chemistry 1:439-442.
- FEIST, W., AND R. ROWELL. 1991. Moisture sorption and accelerated weathering of acetylated and methacrylated aspen. *Wood Fiber Sci.* 23(2):136.
- HON, D. N.-S. 1977. Photodegradation of cellulose acetate fibers. *J. Polym. Sci., Polym. Chem. Ed.* 15:725-744.
- . 1991. Photochemistry of wood. Pages 525-555 in D. N.-S. Hon and N. Shiraishi, eds. *Wood and cellulosic chemistry*. Marcel Dekker, New York, NY.
- . 1992. Thermomechanical pulp and light: Photoactivity of α -carbonyl group in solid lignin. *J. Wood Chem. Technol.* 12(2):179-196.
- . 1994. Degradative effects of ultraviolet light and

- acid rain on wood surface quality. *Wood Fiber Sci.* 26(2): 185-191.
- , AND W. Y. CHAO. 1989. Effect of sulfur dioxide on wood surface quality. Pages 1037-1057 in C. Schuerch, ed. *Cellulose and wood: Chemistry and technology*. John Wiley & Sons, New York, NY.
- , AND W. C. FEIST. 1992. Hydroperoxidation in photoirradiated wood surfaces. *Wood Fiber Sci.* 24(4): 448-455.
- AND ———. 1993. Interaction of sulfur dioxide and nitric oxide with photoirradiated wood surfaces. *Wood Fiber Sci.* 25(2):136-141.
- IMAMURA, Y., AND K. NISHIMOTO. 1986. Resistance of acetylated wood to attack by subterranean termites. *Wood Res.* 72:37-44.
- , AND ———. 1987. Some aspects on resistance of acetylated wood against biodeterioration. *Wood Res.* 74:33-44.
- KUMAR, S., D. INDRA, AND S. P. SINGH. 1991. Hygroscopicity and dimensional stability of wood acetylated with thioacetic acid and acetyl chloride. *J. Timb. Dev. Assoc. (India)* 37:25-32.
- LEARY, G. J. 1968. The yellowing of wood by light. Part II. *Tappi* 51(6):257-260.
- LORÅS, V. 1968. Bleaching and stabilizing of flash-dried mechanical pulp. *Pulp Paper Mag. Can.* 69:57.
- MANCHESTER, D. F., J. W. MCKINNEY, AND A. A. PATAKY. 1960. The brightening of groundwood. *Sven. Papperstidn.* 63:669.
- PEILL, P. L. D. 1946. Permanent bleaching of lignocellulosic materials. *Nature* 158:554.
- PLACKETT, D. V., E. A. DUNNINGHAM, AND A. P. SINGH. 1992. Weathering of chemically modified wood: Accelerated weathering of acetylated radiata pine. *Holz Roh- Werkst.* 50:135-140.
- ROWELL, R. M., S. M. TILLMAN, AND R. SIMONSEN. 1986. A simplified procedure for the acetylation of hardwood and softwood flakes for flakeboard production. *J. Wood Chem. Technol.* 6:427.
- SHEEN, A. D. 1992. The preparation of acetylated wood fibre on a commercial scale. Pages 1-8 in D. V. Plackett and E. A. Dunningham, eds. *Proc. Pacific Rim Bio-Based Composites Symposium*. November 1992, Forestry Research Institute, New Zealand. *FRI Bull.* No. 176.
- SINGH, R. P. 1966. Bleaching of groundwood pulp: Investigation of methods based on chemical modification of the woodpulp. *Tappi* 49:281.
- SUIDA, H. 1930. Acetylating wood. *Austrian Pat.* 122, 499.