

PHOTODEGRADATION AND PHOTOPROTECTION OF WOOD SURFACES¹

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ABSTRACT

Photodegradation of southern yellow pine and its protection have been studied. Scanning electron micrographs showed that most of the cell walls on exposed transverse surfaces were separated at the middle lamella region after only 500 h of ultraviolet light irradiation. Fibers at the surface were degraded severely after 1,000 h of irradiation. Half-bordered pits and bordered pits on exposed radial surfaces were severely damaged by ultraviolet light. Enlargement of pit apertures as well as loss of pit domes was observed. However, wood irradiated on tangential surfaces was quite resistant to UV irradiation; only microchecks were observed. The photodegradative effect on wood surfaces can be mitigated by treating with aqueous solutions of chromic acid or ferric chloride. Only relatively small amounts of these chemicals are needed for effective protection. Possible chemistry and mechanisms of degradation and protection are discussed.

Keywords: Scanning electron microscope (SEM), chromic acid, ferric chloride, ultraviolet light, southern yellow pine.

INTRODUCTION

Wood is an extremely durable material that has long been recognized for its versatile and attractive engineering and structural properties (Browne 1960; Feist 1978). Like other biological materials, however, wood is susceptible to environmental deterioration. Weathering of wood caused by the action of sunlight and water is an example of such deterioration. Weathering is a slow surface deterioration, in which only 6 to 7 mm of the outer layer is eroded away in a century (Browne 1960). Changes of appearance (gloss and color), surface roughness, and surface checking, which are a result of weathering, are of paramount importance when the exterior uses of wood materials in the form of siding, decking, railing, etc., are considered.

The surface changes of wood during outdoor weathering are due to the radiation of solar energy, the presence of moisture (dew, rain, humidity, snow), heat, and other atmospheric elements (oxygen, ozone, oxides of carbon and nitrogen). Of these factors, ultraviolet irradiation from the sun and stresses imposed by wetting

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SPECTRAL ENERGY DISTRIBUTION
of Radiated Mercury Lines in
ACE-HANOVIA HIGH-PRESSURE QUARTZ-VAPOR LAMPS

Mercury Lines, Å	Radiated Energy in Watts
13673 (infrared)	1.0
11287	1.3
10140	1.8

5780 (yellow)	3.4
5461 (green)	3.0
4358 (blue)	2.6
4045 (violet)	1.6

3600 (UV)	3.1
3341	0.36
3130	2.3
3025	0.86
2967	0.48
2894	0.20
2804	0.30
2753	0.14
2700	0.14
2652	0.64
2571	0.20
2537	1.10
2482	0.20
2400	0.20
2380	0.12
2360	0.08
2320	0.03
2224	0.03

Lamp Wattage, 200; Lamp Voltage, 125.

FIG. 1. Spectral energy distribution of irradiation energy from the ACE-Hanovia high-pressure quartz mercury vapor lamp.

are the most important contributing to the weathering phenomenon. Ultraviolet light is a particularly degrading influence.

Wood is an excellent light absorber. Almost every chemical constituent (e.g., cellulose, hemicelluloses, lignin and extractives), in wood is sensitive to ultraviolet light with consequential deterioration effect (Gellerstedt and Petterson 1977). Of these chemical constituents, lignin appears to be oxidized and degraded by light very rapidly (Hon 1981a, b, 1975b; Lin and Gierer 1972). However, because of the strong ultraviolet-absorbing characteristic of lignin, it may also function as a shielding agent to protect cellulosic components from photodegradation, by absorbing detrimental ultraviolet energy and by absorbing such energy being transferred from cellulose (Hon 1975b). Fortunately, ultraviolet light does not penetrate wood deeper than 75 μm (Hon and Ifju 1978). Consequently, the interaction of wood and UV light is essentially a surface reaction, in which free radical intermediates generated by light play a major role in surface deterioration and discoloration (Hon and Feist, 1980a, b; Kalnins 1966).



FIG. 2. Cross section of southern yellow pine ($\times 1,000$).

Much work has been done to protect wood surfaces from the adverse effects of weathering (Feist 1978). Recent work at the Forest Products Laboratory in Madison, Wisconsin, has shown that certain inorganic chemicals, such as chromic acid (chromium trioxide in water), when applied as dilute aqueous solutions to wood surfaces, provide substantial protection (Black and Mraz 1974; Feist 1978, 1979).

In this paper, the effect of photoirradiation on wood surfaces studied by using scanning electron microscopy is reported. The objective of this study is to obtain information on the photo-induced deterioration of wood surfaces at ultrastructural levels. Effectiveness of surface protection from light by using two inorganic chemicals, namely chromic acid and ferric chloride, is evaluated and the mechanism of such protection discussed.

EXPERIMENTAL

Materials

Southern yellow pine (*Pinus* spp.) was used for this study. Specimens with microtomed transverse, radial, and tangential surfaces with dimensions of $1\frac{1}{2}$ in³ were prepared for ultraviolet irradiation. For protection studies, specimens with microtomed surfaces were dipped in chromic acid and ferric chloride solutions with different concentrations for 24 h, followed by air-drying prior to ultraviolet irradiation.

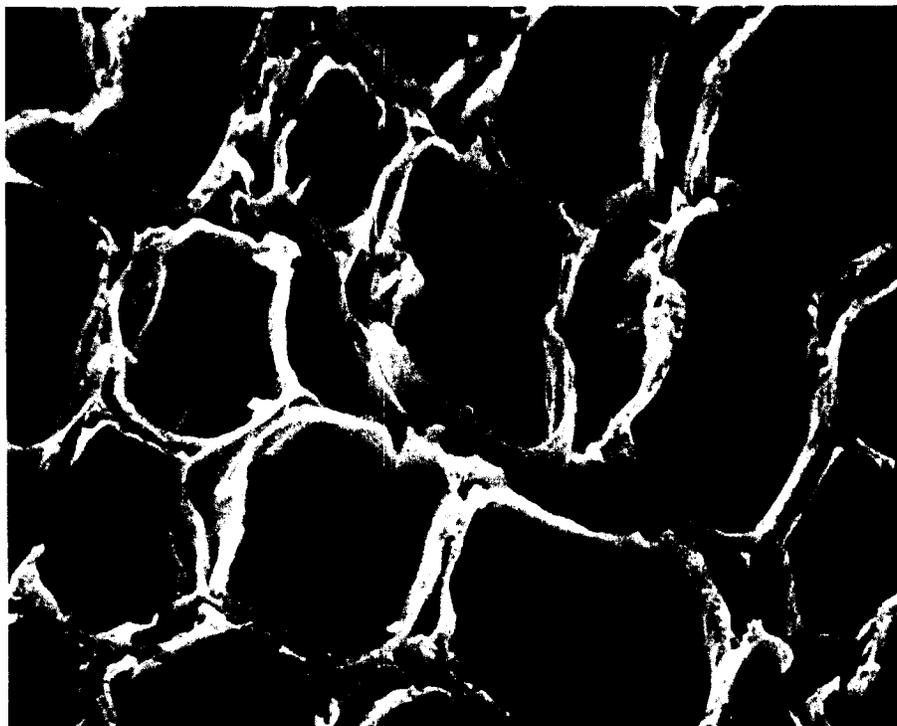


FIG. 3. Cross section of southern yellow pine exposed to ultraviolet light for 500 h ($\times 1,000$).

Methods

The source of ultraviolet light was a high-pressure quartz mercury-vapor lamp (ACE-Hanovia, lamp type 6531-12, 200 W). The relative spectrum energy distribution of the light sources, as given by the manufacturer, is given in Fig. 1. Microtomed specimens were exposed to ultraviolet light directly at a distance of 50 cm for 500 and 1,000 h in a fumed hood with proper ventilation. The surface temperature of the wood during irradiation was about 40 C. Microscopic changes of wood structure after ultraviolet irradiation for treated and untreated specimens were examined through a scanning electron microscope (Advanced Metal Research Corp., Model 900).

RESULTS AND DISCUSSION

Photodegradation of wood surfaces

Deterioration of wood surfaces of southern yellow pine after irradiation by ultraviolet light was readily observed after specimens were exposed for only 500 h. The photodegradative effects on transverse, radial, and tangential surfaces are described below.

Transverse section. The transverse section of southern yellow pine is normally quite simple and homogeneous. Its axial system is essentially composed of wood tracheids with only a relatively small number of parenchyma cells. A scanning

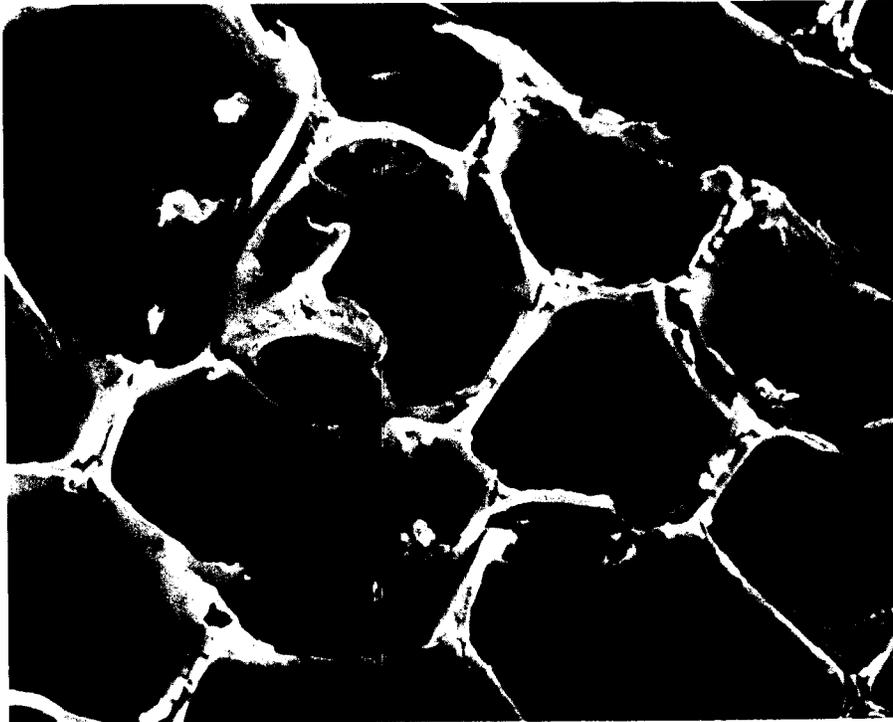


FIG. 4. Cross section of southern yellow pine exposed to ultraviolet light for 1,000 h ($\times 1,000$).

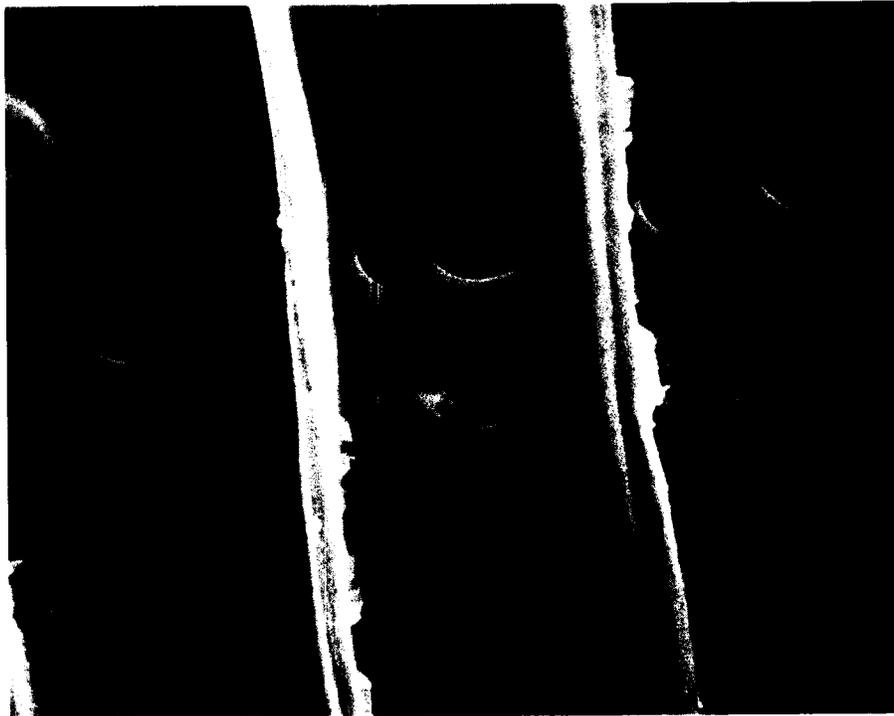


FIG. 5. Simple pit structures of southern yellow pine on radial section ($\times 1,000$).



FIG. 6. Bordered pit structures of southern yellow pine on radial section ($\times 1,000$).



FIG. 7. Deterioration of half-bordered pits and cell wall of southern yellow pine at radial section after exposure to ultraviolet light for 500 h ($\times 1,000$).

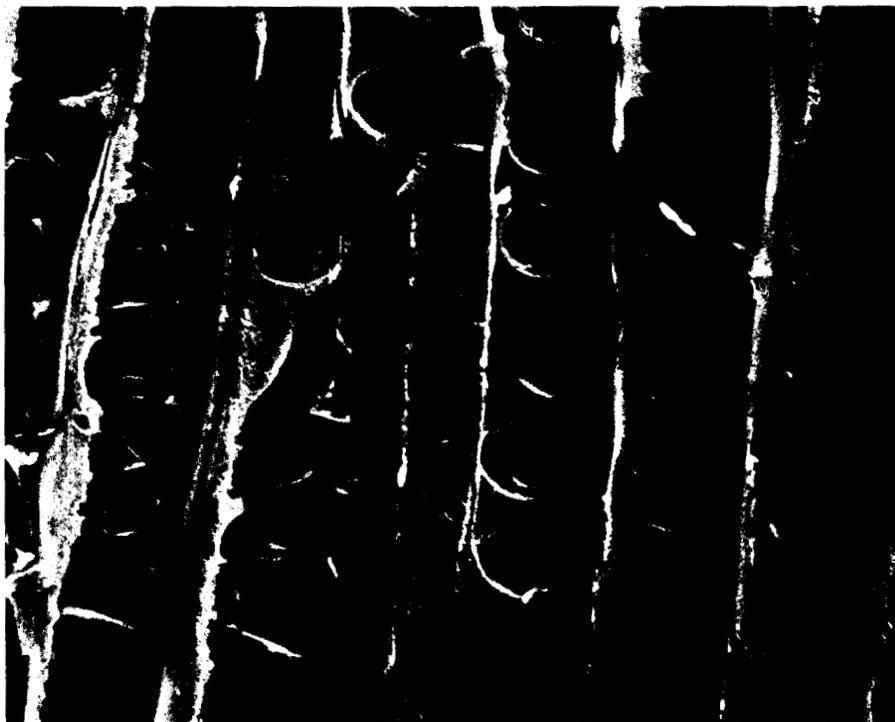


FIG. 8. Deterioration of bordered pits and cell wall of southern yellow pine at radial section after exposure to ultraviolet light for 1,000 h ($\times 1,000$).



FIG. 9. Microchecks of cell wall of southern yellow pine at tangential section (earlywood) after exposure to ultraviolet light for 500 h ($\times 1,000$).

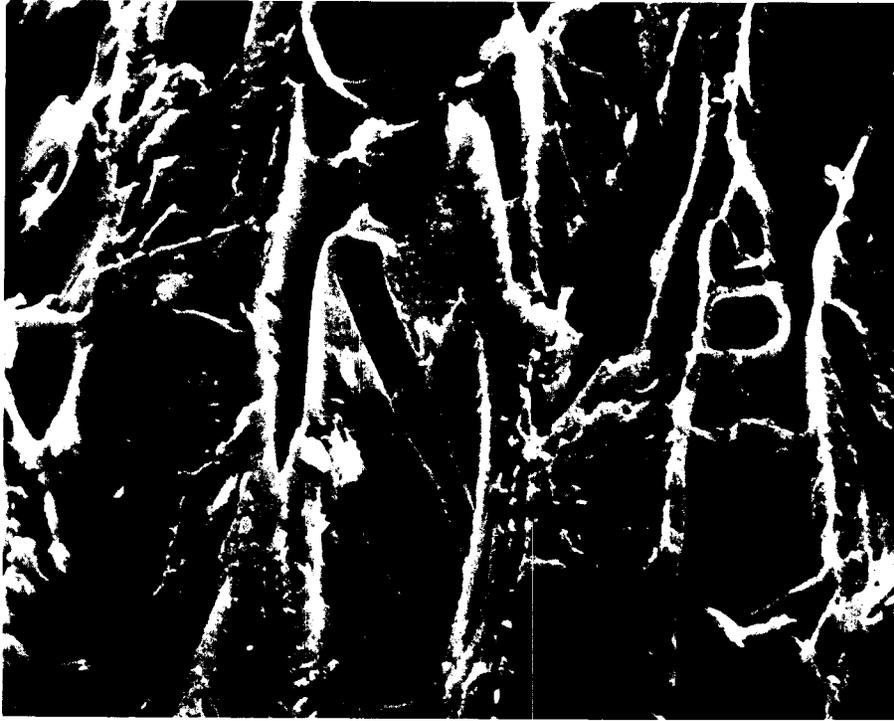


FIG. 10. Microchecks of cell wall of southern yellow pine at tangential section (latewood) after exposure to ultraviolet light for 500 h ($\times 1,000$).

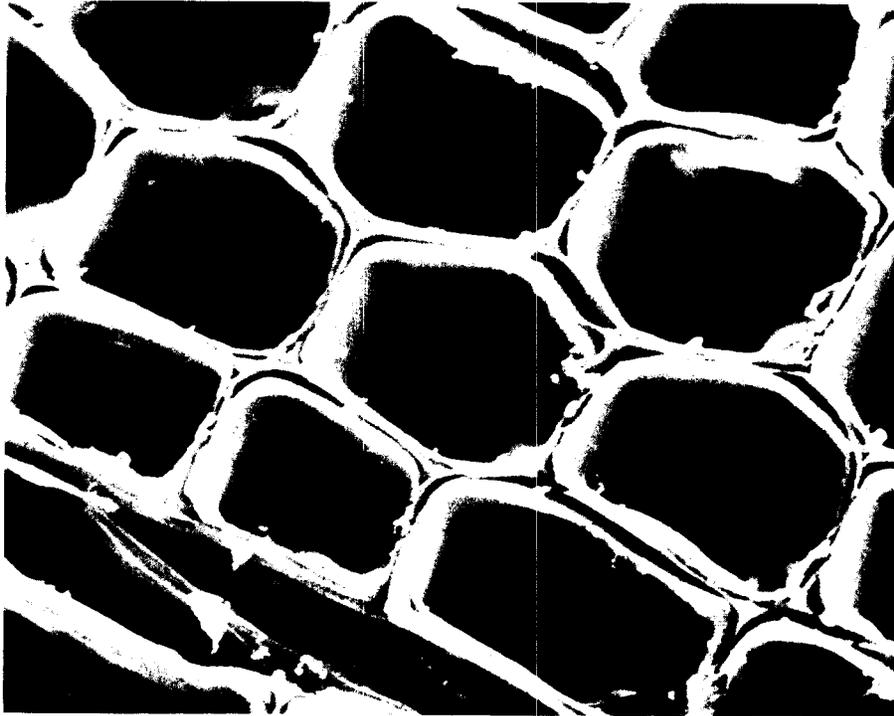


FIG. 11. Cross section of southern yellow pine treated with 0.1% chromic acid solution after exposure to ultraviolet light for 500 h ($\times 1,000$).

electron micrograph (SEM) of a transverse southern pine surface before exposure is shown in Fig. 2.

When the specimen was exposed to ultraviolet light for 500 h, surface deterioration of exposed wood substance was easily observed from the SEM micrograph (Fig. 3). It is obvious that the cell walls were separated at the middle lamella zone. In the extreme case, the secondary wall almost collapsed. Roughening of the surfaces of cell walls could be visually observed. Surface deterioration further developed when specimens were exposed for a total of 1,000 h (Fig. 4). Bordered pits located in the tracheid walls, which can be seen from the transverse section, were totally destroyed. The color of the exposed wood changed from pale yellow to light brown and dark brown after 500 and 1,000 h of UV light exposure, respectively.

Radial section. Bordered pits in southern yellow pine could be observed on radial walls in both earlywood and latewood. Bordered pits located in the earlywood were always larger and more numerous than those in the latewood. Typical SEM micrographs for half-bordered pits and bordered pits on radial walls are shown in Figs. 5 and 6.

The first perceptible change in the anatomical structure of radial sections of southern yellow pine upon photoirradiation appears to be taking place at the pits. After 500 h of ultraviolet exposure, half-bordered pits had strongly interacted with light leading to the damage of pit structure (Fig. 7). Bordered pits also interacted with light, but to a lesser extent. The bordered pits can still be recognized. In addition, checking and void formation in radial walls can occasionally be seen from the photoirradiated specimen. After 1,000 h of exposure, however, severe deterioration of the bordered pits was observed. It can be seen from the SEM micrograph (Fig. 8) that the apertures of bordered pits were enlarged to the limit of the pit chambers, and the pit domes were entirely destroyed. At the extreme, the deterioration also spread over the radial surface of the tracheid wall. It is believed that thorough degradation of these cell walls would probably take place at a longer exposure time. Disappearance of bordered pits has also been observed for redwood irradiated with ultraviolet light (Miniutti 1964, 1967).

Tangential section. Bordered pits were rarely found in these tangential surfaces of those observed. Scanning electron microscope studies revealed that diagonal microchecks passing through bordered pits in tracheid cell walls were the most conspicuous anatomical change on the tangential section upon photoirradiation. The narrow microchecks were oriented diagonally to the axis of the cell wall, indicating that microchecks likely occurred at the fibril angles of S_2 layer of the cell wall (Figs. 9 and 10). A detailed study on ultrastructural change by ultraviolet light has been reported by Miniutti (1967). He suggested that the common appearance of the diagonal microchecks during photoirradiation was the result of local concentrations of tensile stress at right angles to the fibril direction of the S_2 layer. Relatively wider diagonal checks were observed in the tangential section of tracheid walls in latewood (Fig. 10).

Photoprotection of wood surfaces

Certain inorganic chemical treatments have been reported that have the potential to protect wood surfaces from ultraviolet degradation (Feist 1978, 1979). In this study, solutions of chromic acid and ferric chloride were used to treat the

wood specimens before UV exposure. The effectiveness of these treatments in the protection of wood surfaces against photoirradiation was examined by means of scanning electron microscopy. Feist (1979) had demonstrated that wood surfaces treated with chromic acid have enhanced resistance to natural weathering conditions. SEM studies in our investigation substantiated this work. In addition, the effectiveness of photoprotection of wood by ferric chloride was also demonstrated.

Transverse section. SEM micrographs showed that when the specimen was treated with 0.1% chromic acid solution, protective effects can be recognized on transverse surfaces after 500 h of irradiation (Fig. 11). Although some longitudinal microditches² in the middle lamella zone were observed with the chromic acid-treated specimen, the deterioration of cell walls was less, and the microditches narrower, than those of the untreated specimen. The degree of protection was directly proportional to the concentration of chromic acid used in the treatment. When specimens were treated with 5% and 10% chromic acid solution, most of the cell walls were protected (Figs. 12 and 13). The cell walls appeared to be very resistant to photodeterioration; only small voids created at the cell corners were observed after 1,000 h of exposure. The middle lamella region was mostly preserved.

Normally it is believed that ferric chloride is a strong oxidative agent for cellulosic textiles (Hon 1975a); however, a photoprotective effect was observed with wood specimens treated with ferric chloride solution similar to those treated with chromic acid. In addition, similar photoprotective effects of ferric chloride were observed earlier from thermomechanical pulp fibers (Yusoff and Hon 1980).

Radial section. Protective effects of chromic acid and ferric chloride on surface degradation were also observed on radial surfaces. The preservation of both simple and bordered pits by these inorganic salts was readily observed from those treated specimens. At 10% chromic acid treatment concentration, the structure of the pits retained most of their original shape after 1,000 h of ultraviolet irradiation. The diagonal microchecks passing through the bordered pits in radial walls of tracheids, however, still can be observed (Fig. 14).

Tangential section. Both treated and untreated tangential wood surfaces were quite resistant to photoreaction. Frequently observed diagonal microchecks in untreated specimens were minimal in the chromic acid- and ferric chloride-treated specimens (Fig. 15).

These findings show changes in wood microstructure during photodegradation which lead to cell-wall separation at the middle lamella region, and damage of half-bordered and bordered pits on radial surfaces. The degradative effect of ultraviolet light can be minimized by treating wood surfaces with aqueous solutions of chromic acid and ferric chloride.

Chemistry of photodegradation and photoprotection

The occurrence of photochemical reactions at the wood surface greatly depends on the availability of chromophoric groups, e.g., light-sensitive groups in the cell-wall polymers, for ultraviolet light absorption. In general, every chemical component in wood is capable of absorbing light. Of the wood components, lignin is

² This descriptive term was coined by Miniutti when he observed this phenomenon (1967).

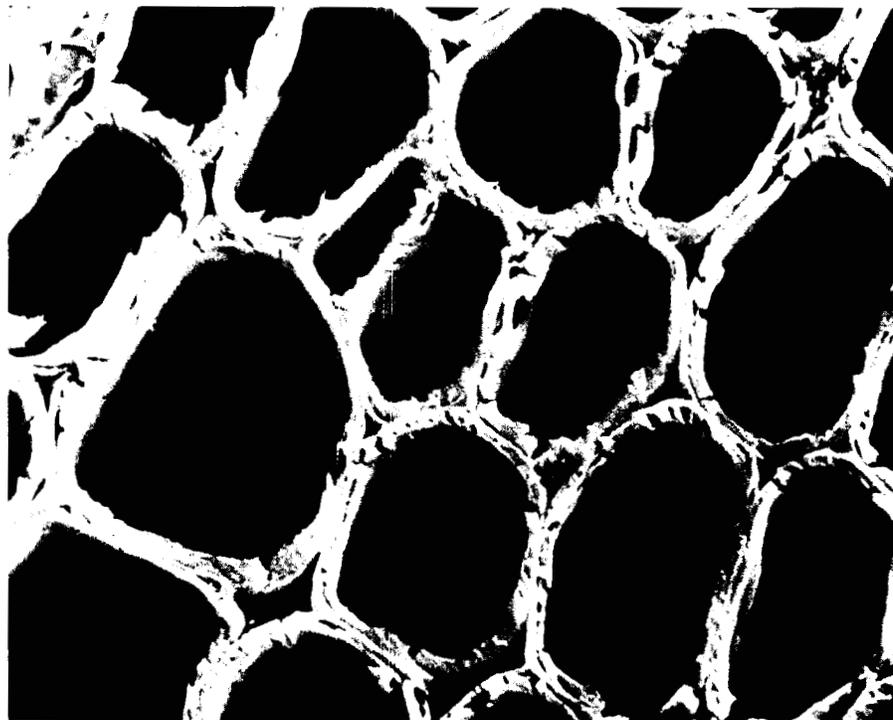


FIG. 12. Cross section of southern yellow pine treated with 5% chromic acid solution after exposure to ultraviolet light for 500 h ($\times 1,000$).

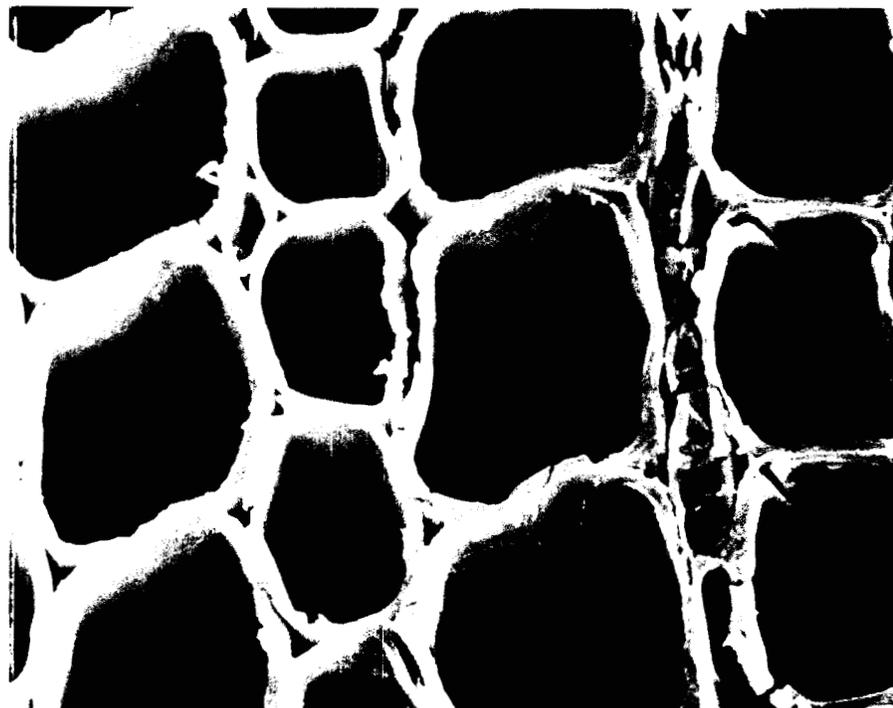


FIG. 13. Cross section of southern yellow pine treated with 10% chromic acid solution after exposure to ultraviolet light for 500 h ($\times 1,000$).



FIG. 14. Microchecks of cell wall of southern yellow pine treated with 10% chromic acid solution after exposure to ultraviolet light for 1,000 h ($\times 1,000$).

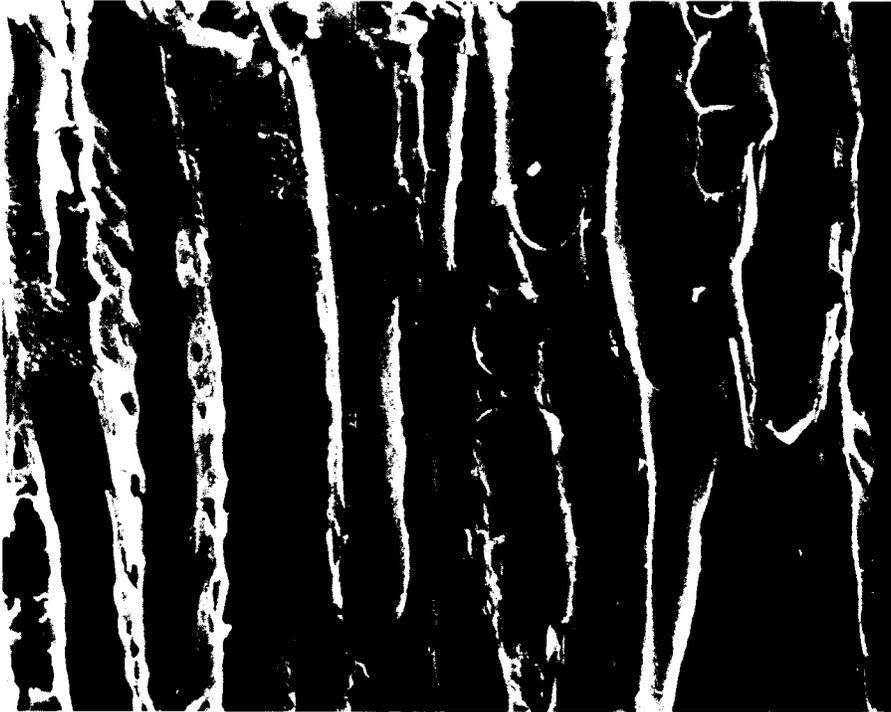


FIG. 15. Tangential section of southern yellow pine treated with 5% ferric chloride solution after exposure to ultraviolet light for 500 h ($\times 1,000$).

the most responsive to interaction with electromagnetic energy because of the phenolic nature of its macromolecular architecture. Degradation and discoloration of lignin by light have been divulged in many papers (Gellerstedt and Petterson 1977; Hon 1981b; Kringstad and Lin 1970; Leary 1967, 1968; Lin and Gierer 1972; Luner 1960). Consequently, it is believed that degradation and discoloration of cell walls are initiated by reactions in the lignin macromolecules. Cellulose and hemicellulose, which are not good light absorbers, are believed to be degraded by light to a lesser extent. Electron spin resonance (ESR) studies also revealed that phenoxy radicals derived from lignin are the principal free radical intermediates produced in wood when exposed to any electromagnetic radiation (Hon et al. 1980). Nature produces lignin in wood to function as a binder to hold together fibers that contain cellulose and hemicellulose. Inasmuch as lignin is degraded by light, it loses its adhesive power; hence, separation of cell walls and the loss of fibrils can be expected. Moreover, cellulose and hemicelluloses at the surface of wood may also interact with light leading to further deterioration. The deterioration and loosening of fibrous materials are the cause of surface roughening.

The incorporation of ferric chloride or chromic acid into wood is able to interfere with the photoreactions and degradation. The exact mechanism of the protection is not clearly understood. In general, it is possible that cellulose and lignin interact with chromium or ferric ions to build up complex systems that are capable of emitting effective energy from wood surfaces. Accordingly, less energy will be absorbed by wood to initiate photoreactions. It is also quite possible that the newly formed complex system between the chemical and wood components would shift the absorbing zone to a shorter wavelength zone. The other possibility is that peroxide impurities, which are potential intermediates leading to discoloration and deterioration, may be produced at wood surfaces as a result of photooxidation. The presence of inorganic salts, which are effective peroxide decomposers, could likely prevent the formation of peroxides at wood surfaces.

CONCLUSIONS

Southern yellow pine is susceptible to ultraviolet light degradation. Most of the cell walls on exposed transverse surfaces were separated at the middle lamella regions after 500 h of irradiation. It appears that the separation of cell walls was due to the degradation of lignin, which interacted strongly with light. Fibers at the surface degraded severely after 1,000 h of irradiation. Half-bordered and bordered pits at the radial surface were severely damaged by light. Enlargement of apertures as well as the loss of pit domes was observed. However, tangential surfaces were quite resistant to UV light, compared to transverse and radial surfaces. Only microchecks were observed at the tangential cell walls.

Ultraviolet degradation of wood surfaces can be abated by treating wood with chromic acid or ferric chloride. SEM studies revealed that the two inorganic salts are capable of protecting wood surfaces against ultraviolet irradiation. The exact mechanism of the protection is not clearly understood. It is speculated that the incorporation of inorganic ions at the wood surface results in wood-ion complex formation, which could interfere with the photochemical reaction either by emitting effective light energy or by shifting the absorbing zone to a short wavelength zone to minimize light absorption. It is also possible that the presence of inorganic

salts would probably decompose peroxide impurities to avoid oxidative chain reactions at wood surfaces.

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