Wood exposed to the outdoors undergoes photodegradation and photooxidation degradation in the natural weathering process. UV light interacts with lignin to initiate discoloration and deterioration. Deterioration of wood in the natural weathering process involves a very complex, free radical reaction sequence. Light does not penetrate wood past .200 µm; therefore, degradation reactions are a surface phenomenon. The free radicals generated in wood by light rapidly interact with oxygen to produce hydroperoxides which in turn are easily decomposed to produce chromophoric groups. In this chapter the influence of outdoor weathering on the performance of wood and wood-based materials is discussed in detail. Macroscopic, microscopic, chemical, and physical changes are described. The mechanisms of weathering and methods of protection of exposed wood surfaces are summarized.

Wood is a naturally durable material that has been recognized for centuries throughout the world for its versatile and attractive engineering and structural properties. However, like other biological materials, wood is susceptible to environmental degradation. When wood is exposed to the outdoors above ground, a complex combination of chemical, mechanical, and light energy factors contribute to what is described as weathering (1). Weathering is not to be confused with decay, which results from decay organisms (fungi) acting in the presence of excess moisture and air for an extended period of time (2). Under conditions suitable for the development of decay,
wood can deteriorate rapidly and the result is far different than that observed for natural outdoor weathering.

The degradation of wood by any biological or physical agent modifies some of its organic components. The organic components in wood are primarily polysaccharides and polyphenolics: cellulose, hemicelluloses, and lignin. Extrinsics are also present in relatively small quantities and their concentration determines color, odor, and other nonmechanical properties of a wood species. A change in these components may be caused by an enzyme, a chemical, or electromagnetic radiation, but invariably, the net result is a change in molecular structure through some chemical reaction. Stalker (3) conveniently divided the environmental agencies that bring about wood degradation into categories. Physical forms of energy were used to describe all factors other than fungi, insects, or animals. The importance of the various physical destructive agents on wood can be considered by comparing two situations, inside and outside the wood structures (Table I). The most serious risk to wood indoors comes from fire. outdoors, the most important factor is weathering.

This chapter updates and consolidates past literature on the weathering and protection of wood, and emphasizes recent and new research in this area.

<table>
<thead>
<tr>
<th>Energy Form</th>
<th>Indoor Result</th>
<th>Degree of Effect</th>
<th>Outdoor Result</th>
<th>Degree of Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal</td>
<td>fire</td>
<td>severe</td>
<td>fire</td>
<td>severe</td>
</tr>
<tr>
<td>Intense</td>
<td>darkening of color</td>
<td>slight</td>
<td>darkening of</td>
<td>slight</td>
</tr>
<tr>
<td>Slight</td>
<td></td>
<td></td>
<td>color</td>
<td></td>
</tr>
<tr>
<td>Light</td>
<td>color change</td>
<td>slight</td>
<td>large color changes</td>
<td>severe</td>
</tr>
<tr>
<td>Visible and UV</td>
<td></td>
<td></td>
<td>chemical degradation (especially lignin)</td>
<td></td>
</tr>
<tr>
<td>Mechanical</td>
<td>wear and tear</td>
<td>slight</td>
<td>wear and tear</td>
<td>severe</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>wind erosion</td>
<td>slight</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>surface roughening</td>
<td>slight</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>delification</td>
<td>severe</td>
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<tr>
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<td></td>
<td>surface roughening</td>
<td>severe</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>deliberation</td>
<td>severe</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>selective leaching</td>
<td>severe</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>color changes</td>
<td>severe</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>strength loss</td>
<td>severe</td>
</tr>
</tbody>
</table>

Table I. Relative Effect of Various Energy Forms on Wood
Background
Perhaps the earliest record of the sun’s effect on wood materials can be found in Exodus 15:23 when Moses led the Israelites into the wilderness of Shur:

And when they came to Marah, they could not drink the waters of Marah, for they were bitter; therefore it was named Marah. So the people grumbled at Moses, saying “What shall we drink?” Then he cried out to the Lord, and the Lord showed him a tree; and he threw it into the waters, and the waters became sweet.

Marah is an area of desert located near the Red Sea on the Sinai Peninsula. The desert water is bitter due to high alkalinity. Weathering of wood on the desert by the sun causes the alcohol groups of cellulose and hemicellulose to be oxidized to carboxyl groups. By throwing a piece of weathered wood into the alkaline water, an acid–base reaction takes place in which the alkalinity of the water is reduced, Thereby, the water becomes sweet.

In addition to this incident, man no doubt was aware of the environment’s degradative effect on wood since he first began using such materials. However, it was not until 1827 that the chemical phenomenon of wood weathering was reported by Berzelius (4), followed by Wiesner (5) in 1846, and Schramm (6) in 1906. However, systematic studies on weathering reactions in wood did not begin until the 1950s (1).

General Aspects of Wood Weathering
In outdoor weathering of smooth wood, original surfaces become rough as the grain raises, the wood checks, and the checks grow into large cracks; grain may loosen, and boards cup and warp and pull away from fasteners. The roughened surface changes color, gathers dirt and mildew, and may become unsightly; the wood loses its surface coherence and becomes friable—splinters and fragments can come off. All these effects, brought about by a combination of light, water, and heat, are comprehended in one word: weathering.

The deleterious effect of wood weathering has been ascribed to a complex set of reactions induced by a number of factors. The weathering factors responsible for changes in wood surfaces are solar radiation (UV, visible, and IR light), moisture (dew, rain, snow, and humidity), temperature, and oxygen. Of these factors, the photon energy in solar radiation is the most damaging component of the outdoor environment and initiates a wide variety of chemical changes at wood surfaces. Moreover, an additional weathering factor has
arisen with the presence of atmospheric pollutants such as sulfur dioxide, nitrogen dioxide, and ozone in the presence or absence of UV light.

**Anatomic Structure of Wood and Its Weatherability.** The cell walls of wood are multilayered. They consist of the middle lamella, primary wall (P), and layers of the outer (S₁), middle (S₂), and inner (S₃) secondary walls. These layers differ from one another with respect to their structures, orientations and number of fibrils or fibers, as well as their chemical composition. The distribution of chemical constituents in the cell walls at the surfaces has a great influence on the weathering stability of wood. The chemical components across the cell wall are depicted in Figure 1. Cellulose, a linear, highly crystalline polymer of (1,4)-β-D-glucopyranose, is the major component of the cell wall (≈45% of total dry weight), and is located mostly in the secondary wall. Hemicellulose (≈20%) is an amorphous, polymeric carbohydrate having a slightly branched structure. Lignin, a three-dimensional network of polyphenols (≈20–30%), is distributed throughout the cell wall but is highly deposited in the middle lamella region. These polymeric materials vary widely in their vulnerability to weathering. The variations in stability are caused primarily by differences in chemical structures, particularly in chromophoric functional groups. Metallic ions and other impurities may also promote deterioration by light (1, 7, 8).

**Weathering Factors.** **Moisture.** One of the principal causes of weathering is frequent exposure of the wood surface to rapid changes in moisture content (1). Rain or dew falling upon unprotected wood is quickly absorbed by capillary action on the surface layer of

![Figure 1. Chemical components across a wood cell wall.](image)
the wood, followed by adsorption within wood cell walls. Water vapor is taken up directly by adsorption under increased relative humidities; consequently, the wood swells. Stresses are set up in the wood as it swells and shrinks due to moisture gradients between the surface and the interior. These induced stresses are greater the steeper the moisture gradient and are usually largest near the surface of the wood. Unbalanced stresses may result in warping and face checking (9-16).

**Light.** The photochemical degradation of wood due to sunlight occurs fairly rapidly on the exposed wood surface (1, 8, 17). The initial color change of wood exposed to sunlight is a yellowing or browning that proceeds to an eventual graying. These color changes can be related to the decomposition of lignin in the surface wood cells and are strictly a surface phenomenon (17–20). These changes occur only to a depth of 0.05–2.5 mm (see section entitled “Penetration of Light and Wood Surface Deterioration”) and are a result of sunlight, particularly UV light, which initiates photodegradation. Photodegradation by UV light induces changes in chemical composition, particularly in the lignin, and subsequent color changes (7, 8, 21–26).

The two most important elements of weathering—sunlight and water—tend to operate at different times. Exposed wood can be irradiated after having been wet by rain or when surface moisture content is high from overnight high humidity or dew. Time of wetness, therefore, is important in relating climatic conditions to exterior degradation. The action of the combined elements can follow different degradation paths, with irradiation accelerating the effect of water or the converse.

**Other Factors.** Heat may not be as critical a factor as UV light or water, but as the temperature increases, the rate of photochemical and oxidative reactions increases (1). Visible light may also contribute to the breakdown of wood during weathering (27, 28). A loss in strength was associated with light-induced depolymerization of lignin and cell wall constituents and to the subsequent breakdown of wood microstructure. The decisive factor in wood weathering in the summer is the intensity of solar radiation, and in the winter the increased amount of SO2 in the surrounding air is the main weathering factor (central Europe exposure) (29).

Freezing and thawing of absorbed water can also contribute to wood checking. Abrasion or mechanical action, such as wind, sand, and dirt, can be an important factor in the rate of surface degradation and removal of wood. Small particles such as sand can become lodged in surface checks and, through swelling and shrinking, weaken fibers in contact with the particles. Solid particles in combination with wind can have a sandblasting effect (1, 8).
Penetration of Light and Wood Surface Deterioration. Although the weathering of wood materials depends on many environmental factors, there is mounting evidence that only a relatively narrow band of the electromagnetic spectrum, i.e., the UV-light portion of sunlight, is responsible for the primary photooxidative degradation of wood.

The first law of photochemistry [the Grotthus–Draper principle (3o)] states that for a photochemical reaction to occur, some component of the system must first absorb light. The second law of photochemistry [the Stark–Einstein principle (31)] states that a molecule can only absorb one quantum of radiation. The absorbed energy causes the dissociation of bonds in the molecules of the wood constituents. This homolytic process produces free radicals as the primary photochemical products. This event, with or without the participation of oxygen and water, can lead to depolymerization and to formation of chromophoric groups such as carbonyls, carboxyls, quinones, peroxides, hydroperoxides, and conjugated double bonds.

Because light must be absorbed before a photochemical reaction can occur, the concentration, location, and nature of chromophores are highly significant in determining the rate of photooxidation of wood. Essentially, wood is an excellent light absorber. Although cellulose is not, it does absorb light strongly below 200 nm with indications of some absorption between 200 and 300 nm, and a tail of absorption extending to 400 nm (32, 33). Because of structural similarity, the UV absorption characteristics of hemicellulose resemble those of cellulose. Lignin and polyphenols absorb light strongly below 200 nm and have a strong peak at 280 nm with absorption down through the visible region (33). Extratives usually have the ability to absorb light between 300 and 400 nm (33, 34). As a consequence, most of the components in wood are obviously capable of absorbing enough visible and UV light to undergo photochemical reactions leading ultimately to discoloration and degradation.

Because of the wide range of chromophoric groups associated with its surface components, wood cannot easily be penetrated by light. Essentially, discoloration of wood by light is a superficial surface phenomenon. The dark brown surface layer of ponderosa pine and redwood that is affected by light extends only 0.5–2.5 mm into the wood (1, 17, 35). As weathering progresses, most woods change to a grayish color, but only to a depth of about 0.10–0.25 mm. Visible (400–750 nm) light as measured spectrophotometrically can penetrate into wood as far as 2540 µm (35). The gray wood surface layer was reported to be 125 µm thick; beneath the gray layer was a brown layer from 508 to 2540 µm thick. These color changes are a result of photochemical reactions that always involve free radicals.
The use of UV light transmission techniques to measure penetration of light through radial and tangential surfaces of different woods as a function of thickness has been reported (36). Electron spin resonance (ESR) techniques were used to monitor free radicals generated underneath different layers of wood. It was found that UV light cannot penetrate deeper than 75 µm; visible light, on the other hand, penetrates up to 200 µm into wood surfaces. Visible light of 400–700 nm is insufficient to cleave chemical bonds in any of the wood constituents (36) because the energy is less than 70 kcal/mol (33, 37). The brown color formed beneath a depth of 508-2540 µm could not be caused by light, as claimed by Browne and Simonsen (35). They suggested that the aromatic moieties of wood components at wood surfaces initially absorb UV light, and that an energy transfer process from molecule to molecule dissipates the excess energy.

The energy transfer processes between electronically excited groups at the outer layer of the wood surface and another group underneath the wood surface account for the photoinduced discoloration of wood underneath the surface, which absorbs practically no UV light. Furthermore, free radicals generated by light are high in energy and tend to undergo chain reactions to stabilize parent radicals. Consequently, new free radicals formed in this way may migrate deeper into wood to cause discoloration reactions.

**Property Changes During Weathering**

**Chemical Changes.** Over a century ago, Wiesner (5) reported that the intercellular substance of wood had been lost because of weathering and concluded that the remaining gray layer consists of “cells that, leached by atmospheric precipitation, have been robbed entirely or in large part of their infiltrated products so much that the remaining membranes consist of chemically pure or nearly chemically pure cellulose.” Similar observations were reported by others (6, 38, 39).

The increase in cellulose content of the weathered wood surface was shown (40) and reported (19). Analytical data on white pine wood that had been weathered outdoors for 20 years was compiled. The results showed that weathering degraded and solubilized lignin. Cellulose appeared to be affected considerably less, except for the top surface layer of the wood. Similar results were obtained with various kinds of wood exposed on a test fence for 30 years. The top gray layer consistently exhibited very low lignin content. The brown layer immediately under the outer gray layer had a lignin content varying from that normally found for fresh unexposed wood by 40–60%. The interior wood layers only a few millimeters under the outer gray surface had a wood composition similar to that of normal, unweath-
ered wood. Analysis of wood sugars from hydrolysis of a water extract of the weathered wood showed that xylan and araban were solubilized more rapidly than was glucosan. Glucose did not predominate in the hydrolyzed water extract during analysis, although glucose units do predominate in unaltered wood polysaccharides.

The UV-degradation process is initiated by the formation of free radicals and presumably begins with oxidation of phenolic hydroxyl (7, 8, 19, 24, 41). This degradation process results in a decrease in methoxyl and lignin content and an increase in acidity and carboxyl concentration of wood substance (see also References 24 and 25). These photochemical changes are enhanced more by moisture than by heat (41). The products of decomposition of weathered wood, in addition to gases and water, are mainly organic acids, vanillin, syringaldehyde, and higher molecular weight compounds, which are all leachable (19, 24). Chemical changes following artificial light irradiation of wood have also been reported by several authors (19, 21–23, 25, 26, 42-45).

Our conclusion is that absorption of UV light by lignin on the wood surface results in preferential lignin degradation. Most of the solubilized lignin degradation products are washed out by rain. Fibers high in cellulose content and whitish to gray in color remain on the wood surface and are resistant to UV degradation.

IR studies revealed that, during UV irradiation of wood, absorption due to carbonyl groups at 1720 cm⁻¹ and 1735 cm⁻¹ increased, whereas the absorption for lignin at 1265 cm⁻¹ and 1510 cm⁻¹ gradually decreased (Figure 2). The increment of carbonyl groups was the result of oxidation of cellulose and lignin. The reduction in the amount of lignin was due to its degradation by light.

A convenient measure of the change in carbonyl groups and lignin is given by the ratio of the IR absorbance bands of carbonyl groups and lignin to the absorption band at 895 cm⁻¹—an absorption band due to hydrogen located at the C-1 position, which is normally unchanged during photoirradiation. Results are shown in Table II. The change in lignin content can also be determined based on a calibration curve of lignin vs. absorption at 1510 cm⁻¹. Results of the change in lignin content at the photoirradiated wood surface are shown in Table III. These results show that carbonyl groups are generated, whereas lignin content is reduced, at the exposed wood surface. Moreover, surface washings of the photoirradiated wood exhibited increasing concentrations of water-soluble oxidation products, which can be detected by UV spectroscopy (Figure 3).

Wood exposed to the outdoors completely lost its absorption at 1265 cm⁻¹ and 1510 cm⁻¹, due to the leaching of degraded lignin,
Figure 2. Change in IR spectra of UV-irradiated wood.

Table II. IR Absorbance of Wood Irradiated with UV Light

<table>
<thead>
<tr>
<th>Irradiation Time (d)</th>
<th>Ratio of Optical Densities</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>1735:895</td>
</tr>
<tr>
<td>0</td>
<td>1.349</td>
</tr>
<tr>
<td>1</td>
<td>1.701</td>
</tr>
<tr>
<td>4</td>
<td>1.871</td>
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<tr>
<td>10</td>
<td>2.164</td>
</tr>
<tr>
<td>20</td>
<td>2.581</td>
</tr>
<tr>
<td>40</td>
<td>2.954</td>
</tr>
</tbody>
</table>
Table III. Change of IR Absorbance and Lignin Content of Wood Irradiated with UV Light

<table>
<thead>
<tr>
<th>Irradiation Time (d)</th>
<th>Absorbance at 1510 cm(^{-1})</th>
<th>Lignin Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.138</td>
<td>28.0</td>
</tr>
<tr>
<td>1</td>
<td>0.131</td>
<td>26.6</td>
</tr>
<tr>
<td>4</td>
<td>0.114</td>
<td>23.4</td>
</tr>
<tr>
<td>10</td>
<td>0.092</td>
<td>19.2</td>
</tr>
<tr>
<td>20</td>
<td>0.076</td>
<td>16.5</td>
</tr>
<tr>
<td>40</td>
<td>0.065</td>
<td>14.5</td>
</tr>
</tbody>
</table>

after 30 d of outdoor weathering (Figure 4). Absorption of carbonyl groups at 1720 cm\(^{-1}\) and 1735 cm\(^{-1}\) was also reduced. This observation shows that the oxidized chemical constituents at the wood surface, particularly lignin components, were moved away from the exposed surface by water. A study of an ionization difference curve of lignin in alkaline conditions revealed that water-soluble fractions of weathered wood exhibited characteristics of phenolic absorption. Electron spectroscopy for chemical analysis (ESCA) studies substantiated that oxidized surfaces have higher oxygen content than carbon.

Figure 3. UV absorption spectra of water-soluble fraction of UV-irradiated wood.
content, thus indicating that weathered wood surfaces are rich in cellulose with carbonyl groups, whereas lignin was degraded and leached away by water (46).

Color Changes. The color of wood exposed to the outdoors is affected very rapidly. Generally, all woods change toward a yellow to brown due to the chemical breakdown (photooxidation) of lignin and wood extratives (1, 5, 7, 17, 47a). This yellowing or browning occurs after only several months of exposure in sunny, warm climates (Figure 5). Woods rich in extratives may become bleached before the browning becomes observable.

When wood is exposed to the outdoors or in artificial UV light for a relatively short period, changes in brightness and color are readily observed. The decreases in brightness and color during 480 d of outdoor weathering are shown in Figures 6 and 7, respectively.
The change of color, $\Delta E$, is based on CIELAB unit (47b). Some wood species, such as redwood, southern yellow pine, and Douglas-fir, lost their brightness significantly in the first month of exposure. These wood species, however, regained their brightness after 180 d of outdoor exposure. Beyond this weathering period, the brightness decreased again. Western redcedar gained in brightness for the first
180 d of outdoor exposure, followed by a decrease in brightness after 180 d of exposure.

In addition to the change in brightness, all wood species exposed to the outdoors changed in color from pale yellow to brown and to gray after 180 d of exposure. As shown in Figure 7, the significant discoloration took place between 90 and 120 d of exposure.

Changes in wood color reveal chemical changes in wood during weathering. Only those parts of the wood close to the exposed surface are affected (see section entitled “Penetration of Light and Wood Surface Deterioration”). As rain leaches the brown decomposition products of lignin, a silver-gray layer consisting of a disorderly arrangement of loosely matted fibers develops over the brown layer (see Chapter 5, Figure 18). The gray layer is composed chiefly of the more leach-resistant parts of the partially degraded wood cellulose. This surface color change to gray is observed when the wood is exposed to the sun in climates with little precipitation. However, another mechanism of surface graying of weathered wood—fungal action—usually predominates, particularly in the presence of moisture.

The discoloration (graying) of woods in the presence of moisture is practically always due to growth of fungi on the surface of the wood (1, 41, 48-52). The most frequently observed fungus species is _Aureobasidium pullulans_ (Pullularia pullulans), which under favorable
conditions grows not only on wood surfaces, but also on the surface of coatings and various organic and inorganic materials (53). This fungus is commonly referred to as mildew. The ecological requirements of this fungus and related fungi are modest, the most important condition for its growth being the sporadic supply of bulk water. The fungus is otherwise relatively resistant and adaptable.

*A. pullulans* grows on finished as well as unfinished or untreated softwood and hardwood surfaces (11). Discoloration of wood by mildew is more general than commonly believed. Fungal infection was the result of wetting the wood surface with water. Twenty European and non-European softwood and hardwood species of widely different density and mechanical strength properties were subjected to unprotected outdoor weathering of wood exposed in Switzerland facing south and inclined at 45° (41). Although behavior among the different species was at first distinctly different, this gradually changed, and photochemical and mechanical deterioration as well as intensity of attack by the blue stain fungi evened out. After only 1 year of weathering, all wood surfaces had a uniformly weathered and gray appearance.

Physical Changes. Weathering of the wood surface due to the combined action of light and water causes surface darkening and leads to formation of macroscopic to microscopic intercellular and intracellular cracks or checks. Strength of cell wall bonds is lost near the wood surface. As weathering continues, rainwater washes out degraded portions and further erosion takes place (Figure 8). Because of the different types of wood tissue on the surface, erosion and checking differ in intensity, and the wood surface becomes increasingly uneven. Hardwoods erode more slowly than do softwoods.

Browne (54) reports that the weathering process is so slow that "only 1/4 inch (6.4 mm) of thickness is lost in a century." However, a value of 1 mm/century has been reported for wood exposed in northern climates (51). An erosion value of 13 mm/century for western redcedar has been reported (55). This value was based on exposure data of 8 years of outdoor weathering at 90° facing south. Erosion data obtained on controlled accelerated weathering of redwood, Douglas-fir, Engelmann spruce, and ponderosa pine were used to estimate outdoor weathering. These data showed that these species would erode at a rate of approximately 6 mm/100 years (a value similar to Browne's) (54). Borgin (56) reported on erosion of wall cladding on stave churches in Norway and estimates that 10-mm-thick cladding had been reduced by 50% over a few hundred years of weathering. Jemison (57) found that ponderosa pine dowels of 5-mm diameter lost 7.8% of their weight after 10 years of exposure in full sunlight; dowels of 13-mm diameter lost 16.4%. Weight losses
Up to 10% were found (58) after heartwood samples of western red-cedar, redwood, iroko, and teak had been weathered for 3 years. Surface profile was found to affect the erosion of wood only insignificantly (59).

The erosion rate of wood exposed to the outdoors has also been
estimated from data obtained by controlled accelerated weathering of several woods (Table IV) (55). Specimens were exposed to a high-density xenon arc light in an accelerated weathering chamber. Exposure was cycles of 20 h of light followed by 4 h of distilled water spray. Erosion measurements were made microscopically (1, 55). The results show that the hard, dense hardwoods erode at a rate similar to that observed for the latewood of softwood species (estimated at 3 mm/century compared to 6 mm for earlywood of softwoods). Generally, the higher the density, the less the erosion rate. Lower density woods, such as basswood, erode at a higher rate than woods such as the oaks, but at a lower rate than the earlywood of softwoods.

Microscopic Changes. Microscopic changes accompany the gross physical change of wood during weathering. The first sign of deterioration in softwood surfaces is enlargement of apertures of bordered pits in radial walls of earlywood tracheids (60–62). Next, microchecks occur which enlarge principally as a result of contraction in cell walls. During weathering, the leaching and plasticizing effects of water apparently facilitate enlargement of the microchecks. Changes were more rapid for redwood than for Douglas-fir.

The scanning electron microscope was used to study the breakdown of the structure of wood due to weathering (56, 63-65). Old wood surfaces, both protected and exposed, were investigated. These studies revealed the slow deterioration and ultimate destruction of the middle lamella, the various layers of the cell wall, and the cohesive strength of wood tissue. Single individual fibers were remarkably stable and durable. The most stable part of the whole fiber seemed to be the microfibril. Various layers of the cell wall failed due to loss of cohesive structure between microfibrils and loss of adhesion between layers. All apertures or voids were enlarged, causing a weakening of the whole fiber structure. The destructive weathering process was limited to a thin surface layer of 2–3 mm. In very old, protected wood there was only a slight breakdown of certain elements at the ultrastructural level, and samples retained their normal macroscopic appearance and properties (65). As long as the main reinforcing structural elements, the microfibrils, remain intact, the major properties of wood do not undergo drastic changes.

Several publications describe the closely related observations of microscopic changes on artificial weathering (UV irradiation) of wood surfaces (45, 60, 62). Changes on the wood surface after accelerated artificial weathering were observed (9) that were very similar to those found for natural outdoor weathering. These changes include the formation of longitudinal checks between adjacent walls of neighboring elements that apparently occur in or close to the middle lamella.
### Table IV. Erosion of Wood Surfaces After Accelerated Weathering

<table>
<thead>
<tr>
<th>Species</th>
<th>Specific Gravity (g/cm³)</th>
<th>600 (h)</th>
<th>1200 (h)</th>
<th>1800 (h)</th>
<th>2400 (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hardwoods</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>White oak</td>
<td>0.641</td>
<td>65</td>
<td>105</td>
<td>135</td>
<td>180</td>
</tr>
<tr>
<td>Red oak</td>
<td>0.566</td>
<td>75</td>
<td>135</td>
<td>150</td>
<td>200</td>
</tr>
<tr>
<td>Maple</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hard</td>
<td>0.572</td>
<td>95</td>
<td>175</td>
<td>200</td>
<td>240</td>
</tr>
<tr>
<td>soft</td>
<td>0.450</td>
<td>85</td>
<td>160</td>
<td>195</td>
<td>250</td>
</tr>
<tr>
<td>Basswood</td>
<td>0.370</td>
<td>130</td>
<td>195</td>
<td>320</td>
<td>385</td>
</tr>
<tr>
<td>Yellow poplar</td>
<td>0.449</td>
<td>115</td>
<td>170</td>
<td>260</td>
<td>305</td>
</tr>
<tr>
<td>Birch, yellow</td>
<td>0.555</td>
<td>100</td>
<td>200</td>
<td>245</td>
<td>300</td>
</tr>
<tr>
<td><strong>Softwoods</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Southern pine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sapwood</td>
<td>0.558</td>
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*Note: Values are for hardwoods and represent heartwood latewood erosion; earlywood erosion was only slightly greater.*

¹ Estimated values
mella, longitudinal checks in element walls, and diagonal checks through pits that probably follow the fibril angle of the S2 layer.

The pattern of breakdown of surface wood cells and cells adjacent to the surface was studied (66, 67) in radiata pine sapwood exposed outdoors to the weather for 4.5 years. The pattern of breakdown was characterized by a progressive deterioration of cells toward the surface. Evidence of deterioration was found 10–12 cells from the surface. The nature of the deterioration was twofold; initial loss of histochemical staining properties of lignin followed by progressive thinning of the cell walls. The thinning of the tracheid walls occurred centrifugally, the inner secondary wall appearing to be lost first.

Deterioration of wood surfaces after exposure to artificial UV light was observed after wood was exposed for only 500 h (68). Photodegradative effects on transverse, radial, and tangential surfaces of a typical southern yellow pine specimen are described in the following sections.

**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. An SEM micrograph of a transverse southern pine surface before exposure is shown in Figure 9.

A microtomed transverse wood face was exposed to UV light for 500 h. Surface deterioration of the exposed wood surface was observed readily from the SEM micrograph (Figure 10). The cell walls were separated at the middle lamella zone. In the extreme case, the secondary wall almost collapsed. Roughening of the surfaces could

*Figure 9. Cross section of southern yellow pine (700 x).*
be observed visually. Surface deterioration further developed when specimens were exposed for a total of 1000 h (Figure 11). Bordered pits located at the tracheid walls were totally destroyed. The color of the exposed wood changed from pale yellow to light brown and then dark brown after 500 and 1000 h of UV light exposure, respectively.

**Radial Section.** Bordered pits in southern yellow pine could
be observed at radial walls in both earlywood and latewood. Generally, bordered pits located in the earlywood were larger and more numerous than those in the latewood. Typical SE M micrographs for half-bordered pits and bordered pits at radial walls before UV exposure are shown in Figures 12 and 13.

The first perceptible change in the anatomical structure of the radial section of southern yellow pine upon exposure appears to take place at the pits. After 500 h of UV exposure, half-bordered pits were damaged. Bordered pits also interacted with light, but to a lesser extent (Figure 14). The bordered pits could still be recognized. In addition, checking and void formation in radial walls occasionally could be seen from the exposed specimen. After 1000 h of exposure, however, severe deterioration of the bordered pits was observed. The SE M micrograph (Figure 15) shows that the apertures of bordered pits were enlarged to the limit of the pit chambers. The pit domes were destroyed completely. At the extreme, the deterioration also spread over the radial surface of the tracheid wall. Complete degradation of these cell walls would probably take place at a longer exposure time. Disappearance of bordered pits has also been observed for redwood exposed to UV light (60, 62).

TANGENTIAL SECTION. Bordered pits were rarely found in the tangential surfaces observed. SE M studies revealed that diagonal microchecks passing through bordered pits in tracheid cell walls were the most conspicuous anatomical change at the tangential section upon UV exposure. The narrow microchecks were oriented diago-

Figure 12. Half-bordered pit structures of southern yellow pine on radial section (700 x).
Figure 13. Bordered pit structures of southern yellow pine on radial section (700 x).

nally to the axis of the cell wall, thus indicating that microchecks occur at the fibril angles of the S₂ cell wall (Figures 16 and 17). Similar observations have been reported (60). The common appearance of the diagonal microchecks during UV exposure was suggested to be the result of local concentrations of tensile stress at right angles to the fibril direction of the S₂ layer. Relatively wider diagonal checks

Figure 14. Deterioration of half-bordered pits and cell wall of southern yellow pine at radial section after exposure to UV light for 500 h (700 x).
Figure 15. Deterioration of bordered pits and cell wall of southern yellow pine at radial section after exposure to UV light for 1000 h (700 x).

were observed in the tangential section of tracheid walls of latewood (Figure 17).

**Weathering of Wood-Based Materials**

The weathering process described thus far has been for solid wood. The introduction of another variable, the adhesive, in the weathering of wood-based materials such as plywood and particle board creates additional complications. Wood substance is still ex-

Figure 16. Microchecks of cell wall of southern yellow pine at tangential section (earlywood) after exposure to UV light for 500 h (700 x).
posed to the elements in these reconstituted products and deteriorates in a manner similar to that for solid wood. The wood–adhesive bond is the new element in exposure (1, 69, 70).

Plywood. The weathering of plywood is related directly to the quality of the veneer exposed and to the adhesives used. Because of its tendency to check, most exterior plywood is protected with a finish or with overlay material. Such plywood weathers and performs similarly to solid wood (1, 2, 71).

The swelling and shrinking that results from periodic wetting and drying plays an important role in weathering by forming checks that expose more wood surface area to weathering. In plywood the checks may expose the glueline to weathering, particularly as they become enlarged by the weathering process (72).

Plywood undergoes many visible changes in appearance during the weathering process. These changes can be described according to the following sequence (72):

1. Large checks that normally originate with lathe checks are first formed. These become wider as weathering along their borders progresses.
2. Microchecks are formed on the surface during the early stages of weathering.
3. The microchecks become deeper, wider, and more and more numerous until they actually separate individual cells and bundles of cells.
4. Particles of degraded wood—cells, cell bundles, and degraded materials—are removed through leaching, volatilization, and mechanical actions; the surface becomes roughened and cratered with a pitted appearance.

5. Lower density areas (earlywood) generally erode more quickly than higher density areas (latewood), thus giving a raised-grain appearance which becomes more and more pronounced as weathering progresses (similar to solid wood).

Because the earlywood of a given softwood species usually weathers away much more quickly than the latewood of that species, the grain pattern of the face ply becomes important in determining the rate at which weathering proceeds to the glueline. Figure 18 illustrates cross-sectional views of weathered plywood at the stage where the exposed, easily weathered earlywood on the face veneer has been eroded away to leave the denser latewood bands exposed. Four different grain patterns have been selected to illustrate their effect on erosion rate. Apparently the glueline can be exposed rapidly when face veneers are taken from either fast-growth trees (Figure 18C) or when they possess a vertical-grain pattern (Figure 18D). When these conditions occur, weathering can proceed directly to the

![Figure 18. Cross-sectional views of plywood illustrating the effects of weathering on face veneers with selected grain patterns.](image-url)
glueline through a path of easily eroded earlywood. The thinner the face veneer, the more probable that a situation such as that depicted in Figure 18C will occur.

Latewood also erodes away through weathering. Its erosion rate for most softwood species is slow (Table IV). Eventually, however, the face veneer of unprotected plywood will erode away, regardless of the grain pattern or wood species.

Reconstituted Panel Products. As in the case of plywood, durability of reconstituted panel products such as hardboard and particle board (waferboard, flakeboard, chipboard, oriented strand board) in outdoor weathering depends very much on wood species and on the amount and nature of resin (binder, adhesive) used in preparing the board (1, 73). Hardboard is generally never exposed directly to the weather. However, it is not unusual for particle boards to be exposed to the outdoors where their outer layers are subjected to greater degradation than the inner layers. As long as the outer cover layers are intact, inner layers are protected from the elements of weathering, When outer layers of exposed boards deteriorate and loosen, and shrinking and swelling of the inner layers result from changes in moisture content. Accelerated deterioration of inner layers generally results, cohesion is lost, and boards may fail under mechanical loads (1). Only 1 or 2 years of weathering can cause significant strength loss and increased swelling (74). Deterioration of particle board during outdoor weathering takes place because of the combined effects of springback from compression set, deterioration of resin, and differential shrinkage of adjacent wood particles during moisture content change. Phenolic resins appear to give the best overall performance. Additional related studies have reported on the effect of natural outdoor and artificial accelerated weathering on durability and strength properties of particle board and related materials (1).

Weathering of Chemically Modified Woods

The chemical modification of wood can play a very important role in controlling the natural weathering process. Researching the effects of chemical modification of wood on weatherability and elucidating the mechanism(s) of UV degradation of modified woods have been undertaken (75, 76). Chemical modification of wood cell walls with butyl isocyanate or butylene oxide, lumen-filling modification with methyl methacrylate, and combined cell wall modification and lumen-filling modifications were compared to unmodified southern pine. Physical, microscopic, and chemical changes occurring on the wood surfaces after UV irradiation in controlled accelerated weath-
ering environments were evaluated for earlywood and latewood. Both UV light and UV light-water combinations of exposure were included in the studies.

The earlywood and latewood of southern pine chemically modified with butyl isocyanate or butylene oxide were not resistant to the degradative effects of UV light. Surface deterioration, color changes, and small weight losses occurred during accelerated weathering (UV light and water spray). Accelerated weathering produced little surface erosion until water washed away degraded wood elements. Degradation and loss of latewood during accelerated weathering was much less than that found for earlywood. This was characteristic of unmodified wood as well. Latewood erosion was greater for butylene oxide-modified wood than all others. Weight loss increased markedly as lignin degradation products were washed away by water, and chemical modification did not reduce this weight loss. Increasing the dimensional stability of the wood and blocking lignin phenolic hydroxyl groups apparently was not enough to stop the extreme degradative effects of UV light in the weathering process. UV absorbers or screens chemically bound may be necessary to protect the exposed wood surfaces.

Lumen-filling modification with methyl methacrylate polymer reduced the extent of erosion. The erosion rate of earlywood and latewood and wood substance loss during accelerated weathering was reduced significantly when compared to chemically modified or unmodified wood. In UV-light exposure, even with water spray action, degradation was minimal. The methyl methacrylate polymer, polymerized in situ within the wood structure, probably reduced water uptake and retarded subsequent leaching of wood degradation products. The polymer can be regarded as a gluelike material holding the surface wood fibers in place even though the natural glue (native lignin) had been degraded on the wood surface by the action of the UV light. As the methacrylate polymer holds the cellulose-rich fibers on the wood surface, the fibers may act as partial screens to protect the underlying wood substance.

Although chemical modification with butyl isocyanate or butylene oxide was not successful in controlling UV light degradation of wood, a combination of either of these chemical modifications with methyl methacrylate lumen-fill treatment resulted in a modified wood that had good resistance to accelerated weathering. The combination of the lumen-filling polymer and the cell wall-modifying chemical treatments provided a dimensional stabilization that significantly increased weatherability. Weight losses for these combined chemical treatments were at least 50% less than those of the chemically modified specimens, and wood erosion and erosion rates were low.
**Chemical Aspects of Weathering Reactions**

Sunlight, especially a small portion of UV light, is the principal instigator of weathering reactions. The immediate consequence of the interaction of wood with light is the generation of free radicals at the exposed surface (7, 19). As these labile free radicals terminate and stabilize, chromophoric and auxochromic groups are formed and discoloration and deterioration occur.

Wood does not contain any intrinsic free radicals (77). However, wood is a good light absorber. It interacts readily with electromagnetic radiation with wavelengths equal to or shorter than visible light and various types of free radicals are generated. They can be detected by electron spin resonance (ESR) spectroscopy (77b). Typical ESR signals of free radicals originating from wood irradiated with different light sources, i.e., fluorescent light, sunlight, and UV light, are shown in Figure 19. The shorter wavelength and greater light energy of UV light generate the highest amount of free radical concentration on the wood surface. This is followed by sunlight and fluorescent light when wood is irradiated under identical conditions. Regardless of the light source, the free radicals formed rapidly interact with oxygen molecules to generate thermal and light sensitive hydroperoxide via a hydroperoxide radical intermediate. This has an adverse effect on wood stabilization against weathering (78). The hydroperoxide impurities generated at wood surfaces can be determined by spectrophotometric techniques using iodometric and triphenylphosphine methods (79, 80).

Free Radical Reactions in Cellulose and Hemicellulose.

The light sensitivity of cellulose has been recognized for nearly a century. In 1883, Witz showed that the photodegradation of cellulose is chemical in nature (81). Free radical intermediates are produced in cellulose during photodegradation reactions, and most of them have been identified (7). The photodegradation rate of cellulose and hemicellulose depends markedly on the intensity and energy distribution of the light, The formation of free radicals is a sign of initiative degradation of the polymer.

Pure cellulose is not influenced in vacuo by the irradiation of light longer than 340 nm, and cellulose degradation by light is confined to a narrow band of the electromagnetic spectrum. However, in the presence of air (mainly oxygen), cellulose degradation may take place at a slow rate when exposed to light of wavelength longer than 340 nm. When cellulose is subjected to sunlight, the glycosidic linkages are cleaved which causes a loss of strength and of degree of polymerization. The formation of free radicals located due to the chain scission at the C-1 and C-4 positions can be detected by ESR spectrophotometry. Discoloration and formation of hydroperoxide on exposed surfaces can be recognized easily.
When cellulose is exposed to light of wavelength longer than 280 nm, in addition to chain scission, dehydrogenation takes place, preferentially at the C-1 and C-5 positions. Dehydroxymethylation due to the cleavage of the C-5–C-6 side chains of cellulose is observed when cellulose is exposed to light longer than 254 nm (82). The formation of carbon radicals, alkoxy radicals, formyl radicals, and hydrogen atoms in cellulose irradiated with various light sources can be detected by ESR. The degree of degradation with different light sources can be evaluated by the change of viscosity, the loss of degree of polymerization, and weight loss.
In general, alkoxy radicals generated in cellulose are stable as compared to carbon radicals. The carbon radicals readily undergo secondary termination reactions. Carbon radicals in vacuo have an affinity for recombination and hydrogen abstraction to stabilize themselves in the presence of oxygen, and they are transformed rapidly into hydroperoxide radicals to build up hydroperoxide. This rapid oxygenation reaction is further accelerated when excited oxygen is present (83).

Although cellulose is not sensitive to UV light of wavelengths longer than 340 nm, the presence of metal ions, particularly ferric ions, dyes, and many sensitizers, promotes free radical formation even when cellulose is exposed to light longer than 340 nm (84). In addition to wavelengths, other factors that have significant effect on free radical formation and degradation rate are oxygen and sensitizers, humidity and wetness (85), and morphology (86a).

**Free Radical Reactions in Lignin.** The conventional lignin model gives a broad picture of the reactive groups available in native lignin that make it an excellent light absorber. Lignin has an absorption peak at 280 nm with its tail extending to over 400 nm (Figure 20). The reactive groups available in lignin consist of ethers of various types, primary and secondary hydroxyl groups, carbonyl groups, and carboxyl groups. There also exist a number of aromatic and phenolic sites and activated locations capable of interacting with light to initiate free radical chain reactions. Because of the complexity of the lignin structure, identifying the free radical sites formed is extremely
difficult. However, with careful selection of model compounds, detailed study of photoinduced free radicals has been possible (7).

Several facts on photochemical reactions have been elicited. They are summarized as follows:

1. Lignin is degraded easily by light of wavelength shorter than 350 nm. Significant color buildup or formation of chromophoric groups is recognized.
2. Lignin is not degraded by light longer than 350 nm, but photobleaching or whitening of lignin can be observed when it is exposed to light longer than 400 nm.
3. Reduction of methoxy content of lignin occurs.
4. Phenoxy radicals are produced readily from phenolic hydroxy groups.
5. Carbon–carbon bonds adjacent to α-carbonyl groups are photodissociated via the Norrish Type I reaction (86b).
6. The Norrish Type I reaction does not occur efficiently in those compounds with ether bonds adjacent to the α-carbonyl group. Photodissociation takes place at the ether bond.
7. Compounds bearing benzoyl alcohol groups are not susceptible to photodissociation except when photosensitizers are present.
8. α-Carbonyl groups function as photosensitizers in the photodegradation of lignin (7).

Because of the phenolic hydroxy groups and ether bonds in lignin, the phenoxy radicals are the major intermediate formed in photoirradiated lignin. Although phenoxy radicals are rather stable intermediates, they are capable of being excited by light, or reacting with oxygen to induce demethylation of the guaiacyl unit of lignin to produce o-quinonoid structures. Leary suggested that o-quinone is the end product of the reaction (87). Consequently, quinonoid moieties formed in lignin are apparently the major chromophoric groups contributing to the discoloration of lignin and wood materials.

Free Radical Characteristics and Reactions in Weathered Wood. Wood, wood fiber components, and isolated lignin contain certain amounts of free radicals that are detectable by ESR spectroscopy (88, 89). Unexposed green wood with 69% moisture content (in dark and in vacuo) was found (77a) to contain no free radicals. A trace amount of free radicals may be produced in the presence of oxygen, and most of these free radicals are generated in wood during mechanical preparation (90) as well as in wood exposed to electromagnetic irradiation. ESR studies revealed that wood interacts readily
with sunlight, fluorescent light, and artificial UV light to produce free radicals, either in the presence of air or in vacuo (Figures 21 and 22). Higher amounts of free radicals were generated in vacuo than in air for all light sources at 77 K. Oxygen is a mandatory element to activate wood surfaces for promoting free radical formation when fluorescent light is used at ambient temperature. For all systems, free radicals generated in vacuo have a relatively long lifetime compared to those generated in the presence of air. Addition of oxygen to wood treated in vacuo promotes free radical formation; peroxo radicals are formed readily at the wood surface. The peroxy radical also seeks to complete its unsatisfied valence, which it may do by abstracting a proton from a nearby molecule to form a hydroperoxide. The hydroperoxide is relatively unstable toward heat and light, and is usually transformed into a new chromophoric group, such as a carbonyl or carboxylic group.

Effect of Water and Moisture on the Formation and Stability of Free Radicals. Water is considered to be a critical element in wood's weatherability, because water is a polar liquid it readily penetrates and swells the wood cell walls. Water molecules may interact with free radicals generated by light. In order to study the influence

![Figure 21. ESR signal intensity (recorded at 77 K) of wood as a function of irradiation time and storage time at ambient temperature. Key: 1, vac. control; 2, vac. fluorescent lamp; 3, air. control; 4, air. fluorescent lamp; 5, vac. sunlight; and 6, air, sunlight.](image-url)
of water molecules upon the reactivity of free radicals, wood with different moisture contents was prepared and exposed to fluorescent light. Different levels of ESR intensity (91), which are directly proportional to free radical concentration, were obtained from the wood. The ESR intensity (either in vacuo or air) initially increased as the moisture content increased from 0 to 3.2%, and reached a peak at 6.3%. At 15.9% moisture content, a significant decrease in intensity was observed. At 31.4% moisture content, only a weak signal was detected (Figure 23). From the stereotopochemistry point of view, the principal role of water is to facilitate light penetration into the accessible regions and to open up the nonaccessible regions for light penetration. Thus, more free radicals are generated in these regions. The excess water molecules present probably trap free radicals to form wood free radical-water complexes (91).

Participation of Singlet Oxygen in the Weathering Process. In addition to sunlight and water, oxygen molecules are among the most ubiquitous in nature. They play a unique role in many photophysical
and photochemical processes. We have explained that oxygen is an important element to promote free radical formation, and possibly that peroxide impurity is formed due to the interaction of free radicals and oxygen molecules. However, the rate of oxidation of most polymers is usually very small without radiation at ambient temperature. The acceleration of the reaction rate by electromagnetic energy may be due to the generation of excited oxygen species. Considerable

![Graph showing ESR relative signal intensities](image)

**Figure 23.** Comparison of ESR relative signal intensities (carried out in a vacuum) of free radicals in earlywood with different moisture contents. Key: SYP, southern yellow pine; WRC, western redcedar; DF, Douglas-fir; and RW, redwood.
evidence exists that many photooxidation reactions involve the low-lying singlet state of oxygen ($^{1}\Delta_g$ and $^{1}\Sigma_g^+$) as intermediates (92).

Wood is a polymer blend containing cellulose, hemicellulose, lignin, and extratatives. These wood components contain internal chemical entities such as carbonyl, carboxyl, aldehyde, phenolic hydroxyl, and unsaturated double bonds, and external entities such as wax, fat, and metal ions. The absorption of light energy by these components may bring them to an excited triplet state that transfers the energy to triplet ground state oxygen molecules to create singlet oxygen (7, 8, 78, 83). The participation of singlet oxygen in the photooxidation of wood was evidenced by using singlet oxygen generators and singlet oxygen quenchers during irradiation. Iodometry studies revealed that hydroperoxide was formed in wood photoirradiated in the presence of oxygen. The formation rate of hydroperoxide at the wood surface increased when methylene blue and rose bengal solutions were added to the wood prior to irradiation (Figure 24). Peroxide radicals involved in the interim were detected by an ESR spectrophotometer, i.e., an asymmetric singlet signal of peroxy radicals with the average g-value of 2.021 ($g_\perp = 2.034; g_\parallel = 2.007$) was detected. On the other hand, when singlet quenchers, such as triethylamine and 1,4-diazabicyclo[2.2.2]octane (DABCO) were used in the identical experiment conditions, the hydroperoxide content was reduced in some cases, even in the presence of rose bengal (Figure 24).

Figure 24. Effect of oxygen and rose bengal on the rate of peroxide formation in wood photoirradiated for 24 h.
This evidence supports the theory that a singlet oxygen is formed during photoirradiation and that it interacts rapidly with free radicals of wood to produce hydroperoxides. Due to the instability against heat and light, the hydroperoxides decompose rapidly under ambient conditions to create chromophoric groups, such as carbonyl and carboxyl groups. These groups contribute to the discoloration of wood surfaces.

Summary of the Chemical Aspects of Weathering. The deterioration of wood materials upon weathering involves a very complex reaction sequence. Penetration of UV light into wood does not traverse deeper than 75 µm. Nonetheless, wood surface reactions initiated or accelerated by light can be observed by discoloration, loss of brightness, and change in surface texture after artificial UV light irradiation or long-term solar irradiation.

Free radical species are generated in wood readily by light. These radicals rapidly interact with oxygen to produce hydroperoxide impurities that are decomposed easily to produce chromophoric groups such as carbonyl and carboxyl groups. The use of singlet oxygen generators, such as rose bengal and methylene blue, as well as singlet oxygen quenchers, such as 1,4-diazabicyclo[2.2.2]octane and triethylamine, suggests the participation of singlet oxygen as an effective intermediate in photooxidation reactions at the wood surface. The presence of water in wood also influences the rate of free radical formation. When moisture content in wood is increased from 0% to 6.3%, more free radicals are formed; beyond this stage, the rate of
radical decay increases. IR studies reveal that carbonyl groups are generated in cellulose and lignin. Water-soluble fractions of degraded wood exhibit characteristics of phenolic absorption due to the loss of lignin. ESCA studies show that oxidized wood surfaces contain higher oxygen contents than unexposed wood surfaces. A general mechanistic scheme, able to account for the weathering, or more commonly photooxidation, of wood surfaces, is illustrated in Figure 26. Free radical chain reactions in the presence of oxygen and light are responsible for the discoloration and deterioration of wood surfaces.

Figure 26. Mechanisms of photodegradation of wood.

Protection Against Weathering

Paint and other coatings on wood (finishes) used indoors can protect and last for many decades without refinishing (93, 94). Indoor finishes are relatively unaffected by wood properties. The durability of finishes on wood exposed outdoors to the natural weathering process, however, depends first on the wood itself. Wood properties that are important in finishing are moisture content; density and texture; resin and oil content; width and orientation of growth rings; and defects such as knots, reaction wood, and fungi-infected (diseased) wood (95). Other contributing factors are the nature and quality of the finish used, application techniques, pretreatments, the time between refinishing, the extent to which the surfaces are sheltered from the weather, and climatic and local weather conditions (96-99).

The primary function of any wood finish is to protect the wood surface from the natural weathering elements (sunlight and water) and help maintain appearance (2). Where appearance does not matter, wood can be left unfinished to weather naturally, and such
wood will often protect the structure for an extended time (1, 2, 54). Different finishes give varying degrees of protection to the weather (96, 97).

Surface treatment provides protection against light and water and will be affected by the weather resistance of the bonding agents of the finish (drying oils, synthetic resins, latexes, etc.). These bonding agents are subject to photodegradation to some degree. The mechanism of failure of paints and other finishes has been described (93, 100), and will not be discussed further here. Wood exposed to the outdoors is protected from the effects of weather by various finishes, by construction practices, and by design factors (2, 11, 96, 97, 101, 102).

Two basic types of finishes (or treatments) are used to protect wood surfaces during outdoor weathering: those that form a film, layer, or coating on the wood surface, and those that penetrate the wood surface to leave no distinct layer or coating. Film-forming materials include paints of all description, varnishes, lacquers, and also overlays bonded to the wood surface. Penetrating finishes include preservatives, water repellents, pigmented semitransparent stains, and chemical treatments.

Film-Forming Finishes, Paints. Of all the finishes, paints most protect wood against erosion by weathering and offer the widest selection of colors. A nonporous paint film will retard penetration of moisture, thereby reducing problems of paint discoloration by wood extratives, paint peeling and checking, and warping of the wood (98, 99). Proper pigments will essentially eliminate photodegradation of the wood surface. Paint, however, is not a preservative; it will not prevent decay if conditions are favorable for fungal growth. The durability of paint coatings on exterior wood is affected by variables in the wood surface, by moisture, and by type of paint.

Paints are commonly divided into the oil-base or solvent-borne systems, and latex or waterborne systems (93, 103). Oil-base (or alkyd) paints are essentially a suspension of inorganic pigments in an oleoresinous vehicle that binds the pigment particles and the bonding agent to the wood surface. Latex paints are suspensions of inorganic pigments and various latex resins in water. Acrylic latex resins are particularly durable, versatile materials for finishing wood and wood-related materials.

Varnishes. The most natural appearance for wood is obtained by use of clear varnishes or lacquers. Other treatments either change wood color or cover it up completely. Unfortunately, clear varnish finishes used on wood exposed to sun and rain require frequent maintenance to retain a satisfactory appearance. Durability of varnish on exposed wood is limited and many initial coats are necessary for
reasonable performance. Maintenance of the varnish surface must be carried out as soon as signs of breakdown occur. This may be as little as 1 year in severe exposures. Lacquers and shellacs are usually not suitable as exterior clear finishes for wood because of water sensitivity and ease of cracking or checking of their rather brittle films.

The addition of colorless UV light absorbers to clear finishes has found only moderate success to help retain the natural color and original surface structure of wood (1, 18, 104–108). Opaque pigments found in paints and stains generally provide the most effective and long-lasting protection against light (1, 42, 109–111). Even when using relatively durable, clear, synthetic resin varnishes, the weatherproof qualities of the wood–varnish system are still limited because UV light penetrates the transparent varnish film and gradually degrades the wood under it (21, 112, 113). Eventually, the varnish begins to flake and crack off, taking with it fibers of the wood that have been degraded photochemically (51, 60, 114).

Studies for predicting the durability of clear finishes for wood from basic properties have been reported (115, 116) and the relations between composition, water absorption, water vapor permeability, tensile strength, and elongation reviewed. Single and multiple regressions were used to establish the relative importance of the different properties in determining durability ratings on outdoor exposure. The durability of clear phenolics and alkyds can be predicted from water absorption and permeability properties. Tensile strength and mechanical properties are of less importance.

Penetrating Finishes. Water Repellents. A large proportion of the damage done to exterior woodwork (paint defects, deformations, decay, leakage, etc.) is a direct result of moisture changes in the wood and subsequent dimensional instability (1, 11, 117–123). This is discussed in detail in the section on the effect of water. Water generally enters wood through open cracks, unprotected end-grain surfaces, and defects in surface treatments. Although the negative effects of such problems can be avoided, or at least reduced, by proper design or correct choice of materials, it is extremely difficult to stop checks or cracks from appearing where woodwork is subjected to harsh long-term exposure. Even a quality coating often loses its protective qualities because it cannot tolerate the stresses and strains of shrinkage and swelling, especially around joints. Eventually, the coating gives way.

Because of these problems, woodwork exposed to the outdoors should be given a protective treatment that is both water-repellent and water-resistant to decay fungi. Such treatment could be used either as the finish itself or prior to the final finish. Materials developed for such purposes are termed water-repellent preservatives.
(WRP). Generally, they are comprised of a resin (10-20%), a solvent, a wax (as the water repellent), and a preservative [generally pentachlorophenol, but others such as bis(tri-n-butyltin) oxide, copper naphthenate, zinc naphthenate, and copper 8-quinolinolate are used] (1, 11, 118-120).

A great store of information has been accumulated on the effectiveness of WRPs in protecting exterior wood (1, 117–119, 121, 122, 124–129). The treatments can be applied by vacuum impregnation, by immersion (which is preferred), by brush, or by spray application. They improve the performance of many finishes applied over them and add greatly to the durability of exposed wood. Even chipboard or particleboard, which is very susceptible to moisture, can be protected quite effectively against the effects of outdoor exposure by using a WRP pretreatment followed by a diffusion-resistant coating (126,130-133).

The WRP treatments give wood the ability to repel water, thus denying stain and decay fungi the moisture they need to live. Wood surfaces that remain free of mildew fungi retain an attractive “natural” appearance. A WRP reduces water damage to the wood and helps protect applied paint from blistering, peeling, and cracking, which often occurs when excessive water penetrates wood.

A WRP usually contains a fungicide as preservative that kills any surface mildew living on the wood. In many medium-to low-hazard decay situations, preservative may not be needed for successful performance of the water repellent (122). Therefore, restriction of water from wood is of prime importance in improving the durability of exposed wood (117).

STAINS. When pigments are added to water repellent or WRP solutions or to similar penetrating transparent wood finishes, the mixture is classified as a pigmented penetrating stain (1, 2, 124, 134). Addition of pigment provides color and greatly increases the durability of the finish because UV light is blocked. These semitransparent stains permit much of the wood grain to show through; they penetrate the wood to a degree without forming a discrete, continuous layer. Therefore, they will not blister or peel even if excessive moisture enters the wood. The durability of any stain system is a function of pigment content, resin content, preservative, water repellent, and quantity of material applied to the wood surface. Their performance during outdoor exposure has received a great deal of attention (1, 69, 71, 124, 134–137).

Penetrating stains are suitable for both smooth- and rough-textured surfaces; however, their performance improves markedly if applied to roughsawn, weathered, or rough-textured wood (1, 69, 99, 124, 134, 137, 138) because more material can be applied to such
surfaces. They are especially effective on lumber and plywood that does not hold paint well, such as flat-grained and weathered surfaces, or dense species. Penetrating stains can be used effectively to finish such exterior surfaces as siding, trim, exposed decking, and fences. Stains can be prepared from both solvent-base resin systems and latex systems; however, latex systems do not penetrate the wood surface. Commercial finishes known as heavy-bodied, solid-color, or opaque stains are also available, but these products are essentially similar to paint because of their film-forming characteristics. Such stains do find wide success when applied on textured surfaces and panel products such as hardboard. They can be oil-based or latex-based (see also “Natural Wood Finishes”).

Preservatives. Although not classified generally as wood finishes, preservatives in wood do protect against weathering and decay, and a great quantity of preservative-treated wood is exposed without any additional finish (2). There are three main types of preservative: (1) the preservative oils (e.g., coal-tar creosote), (2) the organic solvent solutions (e.g., pentachlorophenol), and (3) waterborne salts (e.g., chromated copper arsenate) (2). These preservatives can be applied in several ways, but pressure treatment gives the greatest protection against decay. Greater preservative content of pressure-treated wood generally results in greater resistance to weathering and improved surface durability. The chromium-containing preservatives also protect against UV degradation (1, 138, 139).

Surface Treatments. Certain inorganic chemicals (especially hexavalent chromium compounds), when applied as dilute aqueous solutions to wood surfaces, provide the following benefits (70, 135, 139–141): (1) retarding degradation of wood surfaces by UV radiation; (2) improving durability of UV-transparent polymer coatings; (3) improving durability of paints and stains; (4) providing a degree of dimensional stabilization to wood surfaces; (5) providing fungal resistance to wood surface and to coatings on the surface; (6) serving without further treatment as natural finishes for wood; and (7) fixing water-soluble extractions in woods such as redwood and cedar, thereby minimizing subsequent staining of applied latex paints.

The most successful treatments investigated were those containing chromium trioxide (chromic acid, chromic anhydrate), copper chromate (mixtures of soluble copper salts and soluble chromates), or ammoniacal solutions of these chemicals. Successful results have been obtained by using zinc-containing compounds (142). Sell et al. (143) described surface treatments with chromium-copper-boron salts. Field weathering tests, leaching tests, and electron-probe microanalysis showed that this treatment was resistant to leaching and weathering.
The coating durability of organolead-treated southern pine in exterior exposure was reported (144). Significant improvement in the durability of a vinyl–acrylic latex and an alkyd paint on treated wood was demonstrated. Improved durability appeared to be independent of the type or concentration of the organolead-treated compounds.

The role of chromium in the treatment of wood has been described in detail (145–148). Wood waterproofing, lignin cross-linking, kinetics of reaction, and kinetic behavior have been studied.

Williams and Feist (149) described the application of electron ESCA techniques to evaluate wood and cellulose surfaces that had been modified by aqueous chromium trioxide treatment, ESCA data showed at least 80% Cr(VI) to Cr(III) reduction on all substrates. Leaching experiments confirmed this reduction to a highly water-insoluble or "fixed" chromium complex on both wood and on filter paper (cellulose). Similar oxidation products were observed with wood and filter paper. These experiments indicate that chromium–cellulose and chromium–lignin interactions are involved in the mechanism of chromium stabilization of wood surfaces.

When wood was treated with 0.1% chromic acid solution, protective effects could be recognized on transverse surfaces after 500 h of UV light irradiation (Figure 27) (68). Although some longitudinal microditches in the middle lamella zone were observed with the chromic acid-treated wood, the deterioration of cell walls was less, and the microditches were narrower than those of the untreated wood. The degree of protection was directly proportional to the con-

![Figure 27. Cross section of southern yellow pine treated with 0.1% chromic acid solution after exposure to UV light for 500 h (700 x).](image-url)
centration of chromic acid used in the treatment. When woods were treated with 5 and 10% chromic acid solution, most of the cell walls were protected (Figure 28 and 29). The cell walls appeared to be very resistant to photodeterioration; only small voids created at the cell corners were observed after 1000 h of exposure. For the most part, the middle lamella region was preserved.

Normally ferric chloride is a strong oxidative agent for cellulosic textiles (150); however, a photoprotective effect was observed with wood treated with ferric chloride solution similar to those treated with chromic acid. Similar photoprotective effects of ferric chloride were observed with thermomechanical pulp fibers (151).

Protective effects of chromic acid and ferric chloride treatments on surface degradation also were observed on radial surfaces. The preservation of both simple and bordered pits in woods treated by these inorganic salts was observed. At a 10% chromic acid treatment concentration, the structure of the pits retained most of the original shape after 1000 h of UV irradiation. The diagonal microchecks passing through the bordered pits in radial walls of tracheids, however, can still be observed (Figure 30).

Both treated and untreated tangential wood surfaces were quite resistant to photodegradation. Frequently observed diagonal microchecks in untreated woods were minimal in the chromic acid- and ferric chloride-treated specimens.

These findings show changes in wood microstructure during photodegradation that lead to cell wall separation at the middle lamellae.

Figure 28. Cross section of southern yellow pine treated with 5% chromic acid solution after exposure to UV light for 500 h (700 x).
mella region and to damage of half-bordered and bordered pits on radial surfaces. The degradative effect of UV light can be minimized by treating wood surfaces with aqueous solutions of chromic acid and ferric chloride.

**Natural Wood Finishes**

Some wood finishes are often applied as so-called natural finishes for wood. Each finish system offers various advantages and disadvan-

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**Figure 29.** Cross section of southern yellow pine treated with 10% chromic acid solution after exposure to UV light for 500 h (700 x).

**Figure 30.** Microchecks of cell wall of southern yellow pine treated with 10% chromic acid solution after exposure to UV light for 1000 h (700 x).
tages for this use. These systems can be classified as film-forming or penetrating finishes. The penetrating finishes can be subdivided further into transparent, semitransparent, and waterborne salts as described earlier. The simplest natural finish, as supplied by nature, is the weathering process.

**Film-Forming.** Varnishes are the primary transparent film-forming materials used for natural wood finishes, and they greatly enhance the natural beauty of wood. Varnishes lack exterior permanence unless protected from direct exposure to sunlight. Varnish finishes on wood exposed to the outdoors without protection will generally require refinishing every 1–2 years.

**Penetrating.** The penetrating finishes are the second broad classification of natural wood finishes. These finishes do not form a film on the wood surface.

**Transparent.** Water-repellent preservatives (WRP) are the most important of the transparent penetrating natural finish systems. Treating wood surfaces with WRP will protect wood exposed to the outdoors with little change in appearance. A clean, golden-tan color can be achieved with most wood species. The treatment reduces warping and cracking, prevents water staining at edges and ends of wood siding, and helps control mildew growth. The first application of WRP may protect exposed wood surfaces for only 1–2 years, but subsequent reapplications may last 2–4 years because the weathered boards absorb more of the finish.

**Semitransparent.** The semitransparent oil-based stains are the second of the penetrating natural wood finishes. These stain finishes provide a less natural appearance because they contain pigment that partially hides the original grain and color of the wood. They are generally much more durable than are varnishes or WRPs, and they provide more protection against weathering. With these stain systems, weathering is slowed by retarding the alternate wetting and drying of wood and the presence of pigments on the wood surface minimizes the degrading effects of sunlight. The amount of pigment in the semitransparent stains varies considerably, and different degrees of protection against UV degradation and masking of the appearance of the original wood surface can be achieved.

Latex stains are also described as semitransparent. These pigmented finishes are generally nonpenetrating and retain the surface texture of the wood but often obliterate the natural wood color.

**Waterborne Salts.** Waterborne inorganic salts are a special group of penetrating finishes. These surface treatments result in a finish similar to the semitransparent penetrating finishes because they change the color of the wood and leave a surface deposit of material similar to the pigment found in the semitransparent stains.
Opaque Stains. Solid color or opaque stains are another classification of finishes sometimes inaccurately described as natural wood finishes. These finishes are high in pigment content and completely mask the color and figure of the wood. Surface texture is retained and these finishes yield a flat appearance. They do protect wood against UV degradation, but tend to perform more like paints in that they do not penetrate the wood surface to any degree.

Protection of Wood-Based Materials

Wood-based panel products for exterior applications often require special finishes and special finishing practices (1, 69, 71, 74, 96). Pretreatments and edge treatments are often required.

Protection of exterior reconstituted panel products (in particular particle board) by surface coatings, treatments and overlays, and subsequent weathering performance, has received considerable attention (1, 11, 74, 133, 153–155, 157–159). Painted and overlaid boards are much more durable than unfinished boards. Addition of wax as a water repellent benefits performance of the boards, but does not protect against water vapor (1, 11, 74).

Outdoor weathering experiments with different surface treatments show that the most important prerequisites for long-term protection are the quality of the finish and the protection of board edges against moisture (1, 11), Complementary construction measures are necessary for good performance, and generally, waterproofing and sealing of the wood surface is imperative. Above a minimum value, the gradient of water vapor diffusion of the coating is only of secondary importance. The visual state of the board and thickness swelling are considered the best criteria for evaluating the protective effect of surface treatments. Surface stability is one of the most important criteria in retaining finish and maintaining satisfactory protection and appearance.

Studies on exterior finishes on plywood and plywood composite panels include coating formulations and accelerated testing (1, 69, 71, 136, 158-162).

Wood-Coating Interactions

Many studies contribute to an overall understanding of wood-coating interactions (1, 13–15, 19, 60, 106). Some studies involve adhesives that interact similarly to coatings. Schneider (163) reviewed much of the early work (before 1970) relating to wood-coating interactions. He concluded that even though there was some clear evidence about the nature of wood–coating interactions, much remained in the realm of speculation and untried theory. Subsequent studies by Schneider (164–168) using electron microscopy, fluores-
cence microscopy, and pyrolysis gas–liquid chromatography techniques have dealt with coating penetration in wood.

Scanning electron microscopes and energy dispersion X-ray analysis techniques have been used (169) to examine the distribution and location of the components of water-based preservatives applied to wood. Subsequently, the selective penetration of anions into the cell wall with the cations remaining in the cell lumen has been shown; iron oxide pigments were completely deposited at the wood surface.

Summary and Future Considerations

All wood materials are sensitive to outdoor weathering. Wood exposed to the outdoors without protection undergoes: photodegradation by UV light; leaching, hydrolysis, and swelling by water; and discoloration and degradation by staining and decay microorganisms. Unfinished wood surfaces exposed to weather change color, are roughened by photodegradation and surface checking, and they erode. Although physical as well as chemical changes occur because of weathering, these changes affect only the surface of the exposed wood.

UV light cannot penetrate deeper than 7.5 µm, and visible light no deeper than 200 µm into wood surfaces. There is a rapid loss of brightness and color change when wood is exposed to UV light or to sunlight outdoors. SEM studies show that most of the cell walls on exposed transverse surfaces are separated at the middle lamella region. Half-bordered and bordered pits on exposed radial surfaces are degraded by UV light severely.

Free radicals are generated at the wood surface during irradiation. The rate of free radical formation is enhanced when moisture content increases from 0 to 6.3%. Electron spin resonance and UV studies on the behavior of free radicals generated and their interactions with oxygen molecules to form hydroperoxides revealed that free radicals and singlet oxygen play important roles in discoloration and deterioration reactions of wood surfaces.

Wood exposed to the weather can be protected by paints, stains, and similar materials. Paints provide the most protection to exposed wood surfaces because they are generally opaque to the degradative effects of UV light and protect wood to varying degrees against water. Paint performance may vary greatly on different woods. Pigmented stains also provide durable finishes for wood exposed to the outdoors. Pretreatments such as water-repellent preservatives or certain inorganic chemicals (chromium compounds) can improve the performance of finishes significantly when applied over treated woods.

Many aspects of wood weathering are not understood completely. A complete understanding of the mechanisms involved in
outdoor weathering would allow the development of new pretreatments and finishes that would greatly enhance durability. The ever-changing wood substrate, with previously unused species and new adhesive–wood combinations introduced at increasing frequency, poses particular challenges to modern wood finishes. A detailed study of the various interactions that affect the performance of wood-derived materials is needed to provide suitable protection for these products when they are used outdoors.

Newer techniques and tools for the study of wood surfaces such as Fourier transform IR spectroscopy, electron spectroscopy for chemical analysis, and electron spin resonance spectroscopy will be able to provide a great deal of insight into the weathering process for both finished or unfinished wood substrates. Use of these techniques will allow in-depth study of treatment of wood surface interactions and the importance of these interactions in ultimate performance.

Understanding the role of chemical modification of wood and wood surface in controlling the outdoor weathering process is significant to the future use of wood exposed to the outdoors. The role of modification will become larger as greater demands are placed on the newer wood-based products. The future of such modification lies in end-product property enhancement. Permanently bonded chemicals that provide UV stabilization, color control, water resistance, and dimensional stability could enhance outdoor performance greatly.

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