

Outdoor Wood Weathering and Protection

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The natural weathering process subjects exposed wood to discoloration and degradation by light, moisture, and staining microorganisms. Physical deterioration consists of surface roughening, checking, and cracking. Chemical deterioration involves a complex sequence of free-radical reactions. However, because light does not penetrate wood past 200 μm , degradation reactions are a surface phenomenon. Consequently, wood can be protected by paints, stains, and similar materials. The influence of outdoor weathering on the performance of wood is discussed here in detail. The chemical and physical changes of wood exposed outdoors are described, and the mechanisms of weathering and methods for protecting exposed wood surfaces are summarized. The studies described here have implications for the preservation of historic structures.

WOOD IS A NATURALLY DURABLE MATERIAL that has long been recognized for its versatile and attractive engineering and structural properties. Wood has immense archaeological importance. Contrary to the misconception that old wood is not sound, wood in a favorable environment can last for centuries (1,2). The tomb of the Egyptian pharaoh Tutankhamen, who ruled in the 14th century B. C., contained wood objects that were in perfect condition when recovered in the 20th century. Some Japanese temples constructed with wood date back 13 centuries. In Lucerne, Switzerland, a covered bridge built in 1440 is still in service, and in the United States, some 950 covered bridges built during the 19th century still remain. Many wood dwellings in the United States are centuries old (Figures 1 and 2).

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Figure 1. Old Fairbanks house at Dedham, MA, built in 1637. Most of the white pine clapboard siding was replaced in 1903, and it has withstood 85 years without paint..

However, like other biological materials, wood is susceptible to environmental degradation. When wood is exposed outdoors above ground, a complex combination of chemical, mechanical, and light energy factors contribute to what is described as weathering (1-3). Weathering can be detrimental to the surfaces and appearance of historic structures. Thus, weathering must be taken into account in a discussion of the preservation and protection of outdoor wood. Weathering of wood is not to be confused with wood decay (rot), which results from organisms (fungi) acting in the presence of excess moisture and air for an extended period (4). Under conditions suitable for decay, wood can deteriorate rapidly, and the result is far different from that observed for natural outdoor weathering.



Figure 2. White oak log cabin near Middleton, WI, constructed around 1845 and never painted or finished.

The degradation of wood by any biological or physical agent modifies some of the organic components of wood (2). These components are primarily polysaccharides (cellulose, hemicelluloses) and polyphenolics (lignin) (Figure 3). Extractives are also present in relatively small quantities, and their concentration determines color, odor, and other nonmechanical properties of a wood species. A change in the organic 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 (5) conveniently divided the environmental agents that bring about wood degradation into categories; all agents other than fungi, insects, or animals are categorized as physical forms of energy. The relative effects of various energy forms on wood, indoors and outdoors, are compared in Table I. The most serious threat to wood indoors comes from thermal energy, and outdoors, from weathering—the combination of chemical, mechanical, and light energies.

Although the degradative effect of the environment on wood has undoubtedly been recognized for centuries, Berzelius (6) first reported the

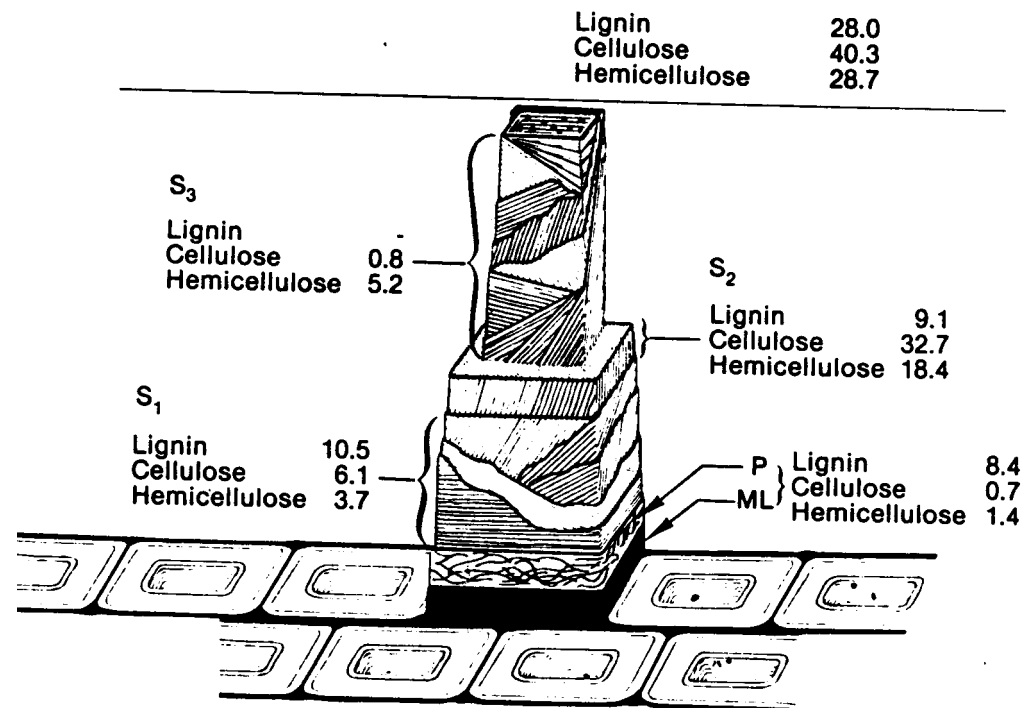


Figure 3. Chemical components in a typical softwood cell wall. Values are given as percentages.

Table I. Relative Effect of Various Energy Forms on Wood

Form of Energy	Indoors		Outdoors	
	Result	Degree of Effect	Result	Degree of Effect
Thermal				
Intense	Fire	Severe	Fire	Severe
Slight	Darkening of color	Slight	Darkening of color	Slight
Light*	Color change	Slight	Extensive color changes	Severe
			Chemical degradation (especially lignin)	Severe
Mechanical	Wear and tear	Slight	Wear and tear	Slight
			Wind erosion	Slight
			Surface roughening	Severe
			Defiberization	Severe
Chemical	Staining	Slight	Surface roughening	Severe
	Discoloration	Slight	Defiberization	Severe
	Color change	Slight	Selective leaching	Severe
			Color change	Severe
			Strength loss	Severe

NOTE: Based on data from ref. 5.

*Both visible and ultraviolet light.

chemical phenomenon of wood weathering in 1827, followed by Wiesner (7) in 1864, and Schramm (8) in 1906. 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 (Figure 4). Other changes may occur. The grain loosens; boards cup, warp, and pull away from fasteners; the roughened surface changes color, gathers dirt and mildew, and becomes unsightly; the wood loses its surface coherence and becomes friable; and splinters and fragments break off the surface. All these effects, which are brought about by a combination of light, water, and heat, are encompassed in weathering.

Surface chemical changes occur very rapidly when wood is exposed to the natural weathering process. Studies on the effect of short periods of weathering before finishing (9, 10) showed that adhesion of both an acrylic latex and an alkyd-oil primer to wood was significantly reduced after the wood substrate had weathered for 4 or more weeks before painting. Reduced paint adhesion and increased failure of the wood-paint interface will inevitably result in poor long-term paint and finish performance. These studies conclude that wood should be protected with a finish that will prevent



Figure 4. Close-up view of 140-Year-old weathered white oak logs of house shown in Figure 2.

photodegradation and water damage if the wood remains outdoors for more than 2 weeks.

Kleive (11) and Underhaug et al, (12) also conducted studies on how the weathering of unpainted wood affects the durability of exterior coatings. These authors demonstrated that the surfaces of spruce and pine wood degraded rapidly when exposed to the weather. After 1 month of outside exposure, the paint-holding properties of the wood were adversely affected. The wood continued to deteriorate throughout the next 6-10 months. Kleive and Underhaug et al, also demonstrated that a good finish performance on weathered wood could be obtained by planing the top layer to at least 1 mm to expose the unweathered wood. Moreover, wood that is porous because of the action of microorganisms should be primed with a very-low-viscosity penetrating primer to ensure saturation of the wood.

Weathering Factors. The deleterious effect of wood weathering has been ascribed to a complex set of reactions induced by a number of factors (2). The weathering factors responsible for changes in the wood surface are as follows: moisture (dew, rain, snow, and humidity), solar radiation (ultra-

violet (UV), visible, and infrared light), temperature, and oxygen. Of these factors, the photon energy in solar radiation is the most damaging, initiating a wide variety of chemical changes at wood surfaces. Moreover, in recent years, an additional weathering factor has arisen because of atmospheric pollutants such as sulfur dioxide, nitrogen dioxide, and ozone in the presence or absence of UV light (13). The following section describes the weathering factors of moisture, light, and acid deposition, as well as other factors such as temperature.

Moisture. One principal cause of weathering is frequent exposure of the wood surface to rapid changes in moisture content (1, 2). Rain or dew falling on unprotected wood is quickly absorbed by the surface layer through capillary action, followed by adsorption within the wood cell walls. Water vapor is taken up directly by the wood by adsorption under increased relative humidities, and the wood swells. Stresses are set up in the wood as it swells and shrinks because of moisture gradients between the surface and the interior. The steeper the gradient, the greater the stress. Stresses are usually the greatest near the surface of the wood. Unbalanced stresses may result in warping and face checking (14-21).

The importance of the effect of water on wood exposed outdoors was demonstrated by Banks and Evans (22), who exposed thin radial sections of scotch pine and lime to deionized water over the temperature range 25-65 °C. Losses in wet tensile strength and toughness occurred rapidly at temperatures ≥ 50 °C. After about 2 months of exposure, the pine lost 10-30% tensile strength and 20-60% toughness. For lime, the losses were somewhat greater: about 20-60% tensile strength and up to 80% toughness. Further exposure for about 18 months led to about 60% tensile strength loss in pine and 80% in lime. Both species lost approximately 90% toughness after this period of exposure. Banks and Evans believe that these phenomena were due purely to physicochemical processes and that the losses in strength may contribute significantly to detachment of paints and other finishes from wood surfaces.

Light. The photochemical degradation of the exposed wood surface from sunlight occurs fairly rapidly (1, 2, 23, 24). The initial color change of wood exposed to sunlight is a yellowing or browning that proceeds to an eventual graying (Figure 5). These color changes can be related to the decomposition of lignin in the surface wood cells. The changes are strictly a surface phenomenon (2, 24-27) and occur to a depth of only 0.05-2.5 mm (see section on penetration of light). Photodegradation by sunlight, particularly UV light, induces changes in chemical composition, especially in lignin, and subsequent color changes (23, 28-34).

Miller and Derbyshire (35-37) showed that visible light may also contribute to the breakdown of wood during weathering. A loss in strength was

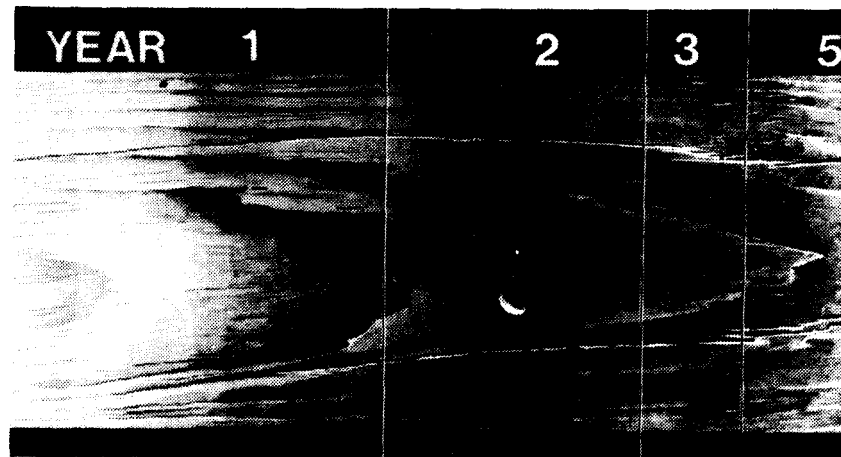


Figure 5. Atrist's rendition of surface color changes during the outdoor weathering process of a typical softwood. Wood initially darkens (yellows or browns) and eventually lightens (grays).

associated with light-induced depolymerization of lignin and cell wall constituents and with the subsequent breakdown of wood microstructure.

The two most important factors of weathering—sunlight and water—tend to operate at different times. The time of wetting is important in relating climatic conditions to exterior degradation of wood. For example, exposed wood may be irradiated while it is wet from rain, dew, or other conditions of high humidity. The action of the combined elements can follow different degradation paths, with irradiation accelerating the effect of water or the converse. The role of water and free-radical generation is discussed in a later section.

Acid Deposition. The attention given to acid deposition (acid rain) during the last decade has prompted interest in the effect of acids on wood weathering (9). Raczowski (38) showed that in the summer, the decisive factor in wood weathering is the intensity of solar radiation, whereas in the winter, it is the increased amount of sulfur dioxide in the surrounding air (central Europe exposure). Williams (39) measured the effect of acid treatment on the erosion rate of western redcedar by using xenon arc accelerated weathering techniques. Test specimens were periodically soaked in nitric and sulfuric acids at different pH levels during accelerated weathering. Compared with the unsoaked controls, specimens treated with acids at pH 3.0 experienced a 10% increase in erosion rate; at pH 3.5, a 4% increase; and at pH 4.0, no increase. The pH levels used in this study were felt to be somewhat conservative because naturally occurring atmospheric acid concentrations have been reported in the range of pH 2.0.

The effects of acid rain on painted materials can be seen in the degra-

dation of the coating and substrate. The type of pigment and extenders used in paint formulations has a direct bearing on paint performance in an acid environment (9). The degradation of the substrate also has a direct bearing on coating performance. Because substrate degradation may induce different coating-failure mechanisms, future research should include the reaction of the substrate-coating interface to acid rain.

Other Factors. Although heat may not be as critical a weathering factor as UV light or water, as the temperature increases, the rate of photochemical and oxidative reactions increases (1, 2). Freezing and thawing of absorbed water can also contribute to wood checking. Abrasion or mechanical action caused by such elements as wind, sand, and dirt can significantly affect the rate of surface degradation and removal of wood. Small particles such as sand can become lodged in surface checks, and the swelling and shrinking of the wood can weaken fibers in contact with these particles. Solid particles in combination with wind can have a sandblasting effect (1, 2, 23).

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 (the UV light portion of sunlight) is responsible for the primary photooxidative degradation of wood.

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 (40, 41). Essentially, wood is an excellent light absorber. Cellulose absorbs light strongly below 200 nm, some absorption occurs between 200 and 300 nm, and a tail of absorption extends to 400 nm (42, 43). Because hemicellulose is structurally similar to cellulose, its UV light absorption characteristics are also similar. Lignin and polyphenols absorb light strongly below 200 nm and have a strong peak at 280 nm, with absorption down through the visible region (43). Extractives usually have the ability to absorb light between 300 and 400 nm (43, 44). In summary, most components in wood are capable of absorbing enough visible and UV light to undergo photochemical reactions that ultimately lead to discoloration and degradation.

Because a wide range of chromophoric groups is associated with the surface components of wood, wood cannot easily be penetrated by light. The discoloration of wood by light is essentially a surface phenomenon. The dark brown surface layer of ponderosa pine and redwood affected by light has been reported to reach only 0.5-2.5 mm into the wood (1, 2, 24, 43). As weathering progresses, most woods change to a grayish color, but only to a depth of about 0.10-0.25 mm. Browne and Simonsen (45) reported that visible (400-750 nm) light, as measured spectrophotometrically, can penetrate into wood as far as 2540 μm . They mentioned that the gray layer of

the wood surface was 125 μm thick, and a brown layer beneath the gray layer ranged from 508 to 2540 μm thick. These color changes are a result of photochemical reactions, which always involve free radicals.

Hon and Ifju (46) reported 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. By using electron spin resonance (ESR) techniques to monitor free radicals generated in different layers of wood, these authors found that UV light cannot penetrate deeper than 75 μm ; visible light, on the other hand, penetrates as far as 200 μm into wood surfaces. Hon and Ifju claimed that visible light of 400-700 nm is insufficient to cleave chemical bonds in any wood constituents. The light energy is less than 70 kcal/mol (43, 47). The brown color formed beneath a depth of 508-2540 μm in wood cannot be caused by light, as claimed by Browne and Simonsen (45). Hon and Ifju suggested that the aromatic moieties of wood components at wood surfaces initially absorb UV light, followed by an energy-transfer process from molecule to molecule to dissipate the excess energy.

The energy-transfer processes between electronically excited groups at the outer layer of the wood surface and groups beneath the wood surface presumably account for the photoinduced discoloration of wood underneath the surface, where practically no UV light penetrates. Furthermore, free radicals generated by light are high in energy and tend to undergo chain reactions to more stable 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 (7) reported that weathering causes loss of the intercellular substance of wood. He 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." Schramm (8), Wislicenus (48), and Mobius (49) reported similar observations.

The increase in cellulose content of the weathered wood surface was shown by Browne (50) in work reported by Kalnins (26). Browne compiled analytical data on white pine wood that had been weathered outdoors for 20 years. Results showed that weathering degraded and solubilized lignin. Cellulose appeared to be considerably less affected, except in 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 outer gray layer consistently exhibited very low lignin content (Table II). The lignin content of the brown layer immediately below this layer varied from 40 to 60% of that normally found for fresh nonexposed wood. The composition of inner wood layers only a few millimeters under the outer gray surface was similar to that of

Table II. Cellulose and Lignin Content of Wood Weathered for 30 Years Outdoors

Sample Type	Wood Type and Species	Wood Component in Different Cell Layers, %					
		Cellulose			Lignin		
		Inner	Middle ^a	Outer ^b	Inner	Middle	Outer
Extracted	Softwood						
	Western redcedar	48	48	44	42	28	7
	Douglas-fir	50	46	47	36	30	7
	Southern pine	51	52	51	50	21	4
	Hardwood						
	Yellow-poplar	51	59	62	27	15	2
Unextracted	Birch	55	57	60	28	21	6
	Softwood						
	Western redcedar	54	47	44	33	27	10
	Douglas-fir	49	50	53	34	29	6
	Southern Pine	52	51	49	31	20	7
	Hardwood						
	Yellow-poplar	50	64	64	22	16	2
	Birch	47	56	70	21	17	4

NOTE: Data from ref. 50.

^aMiddle brown layer.^bOuter gray layer.

normal unweathered 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 glucosan. In addition, glucose did not predominate in the hydrolyzed water extract, although glucose units do predominate in unaltered wood polysaccharides.

Lignin degradation after weathering was demonstrated by analyzing aspen wood samples exposed to accelerated weathering. The 2400 h of artificial weathering was equivalent to approximately 5 years of outdoor exposure. The composition of the exposed wood compared to unexposed wood is described in Table III. The outer weathered layer was scraped away for analysis. Reduced lignin content and a corresponding increase in cellulose content (as shown by an increase in glucose content) was found in the wood surfaces exposed to controlled accelerated weathering (UV light and water). There was an accompanying decrease in xylose and mannose.

Table III. Chemical Composition of Aspen Wood Before and After Accelerated Weathering

Component	Exposed Wood, %	Unexposed Wood, %
Klason lignin	1.9	20.5
Acid-soluble lignin	3.1	5.6
Glucose	82.2	49.8
Xylose	10.1	23.3
Mannose	1.6	4.2

Free radicals, which are generated in wood by UV light during the weathering process, play an essential role in surface deterioration and discoloration. Kalnins et al. (51) investigated the formation of free radicals in wood after exposure to light by the use of ESR. The free radical concentration of wood kept in the dark was very low; it increased when the wood was exposed to daylight, especially UV light. In a vacuum or inert atmosphere, the free radicals were stable, and in the presence of oxygen, they rapidly decomposed.

Wood apparently does not contain any intrinsic free radicals (26, 51, 52). However, free radicals were generated by irradiation of wood with fluorescent light at ambient temperatures (52, 53). Rate of free-radical formation was enhanced when moisture content increased from 0 to 6.3%. The ESR and UV absorption studies on the behavior of generated free radicals and their interaction with oxygen molecules to form hydroperoxides revealed that free radicals and singlet oxygen play important roles in the discoloration and deterioration of wood surfaces. The chemistry of weathering and protection was summarized in a technical publication (2).

The degradation process in wood caused by UV light is initiated by the formation of free radicals and begins presumably with oxidation of phenolic hydroxyl (23, 26, 28, 32, 54). The degradation process results in a decrease in methoxyl and lignin content and an increase in acidity and carboxyl concentration of wood substance (see also 32, 33). These photochemical changes are enhanced more by moisture than by heat (54). The products of decomposition of weathered wood, in addition to gases and water, are mainly organic acids, vanillin, syringaldehyde, and high-molecular-weight compounds, which are all leachable (26, 32). Chemical changes following artificial-light irradiation of wood have also been reported (26, 29-31, 33, 34, 55-58).

Some characteristics of the photochemical reactions in wood (2, 3) are as follows:

1. Lignin is easily degraded by light with a wavelength <350 nm. Significant color buildup or formation of chromophoric groups occurs.
2. Lignin is not significantly degraded by light with a wavelength >350 nm, but photobleaching or whitening of lignin occurs when it is exposed to light >400 nm.
3. Methoxyl content of lignin is reduced.
4. Phenoxy radicals are readily produced from phenolic hydroxy groups.
5. Carbon-carbon bonds adjacent to α -carbonyl groups are photodissociated.
6. Compounds bearing benzoyl alcohol groups are not suscep-

tible to photodissociation except when photosensitizers are present.

7. α -Carbonyl groups function as photosensitizers in the photodegradation of lignin (28).

Work on the chemical changes of weathered wood has indicated that absorption of UV light by lignin on the wood surface results in preferential lignin degradation. Most 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 light degradation.

Free radicals rapidly interact with oxygen to produce hydroperoxide impurities, which in turn are easily decomposed to produce chromophoric groups, such as conjugated carbonyl and carboxyl groups (2, 59, 60). A preliminary study of the sulfate of wood exposed to outdoor weathering and UV irradiation (59) showed that electron spectroscopy for chemical analysis (ESCA) provides valuable information and insight into the manifestation of weathering and photooxidation. From the ESCA spectra, the increase in signal intensities of carbon-oxygen bonds and oxygen-carbon-oxygen bonds (or unsaturated carbon-oxygen bonds) and oxygen-to-carbon ratio, and the decrease in carbon-carbon and carbon-hydrogen bonds of weathered and UV-irradiated wood surfaces demonstrated that the wood surface was oxidized. Only slow oxidation was observed at 100 μm under the exposed wood surface. Oxygen-to-carbon ratio data showed that the weathered wood surface was rich in cellulose but poor in lignin. The leached degradation products from the weathered wood surface accounted for the discrepancy between the ESCA shapes of UV-irradiated and weathered wood surfaces.

Surface characteristics of UV-irradiated wood were analyzed by infrared and UV spectroscopy (60). Analyses of infrared spectra revealed that the UV-irradiated wood is rich in conjugated carboxylic and carbonyl chromophoric groups and poor in aromatic functional groups. Ultraviolet spectral studies suggested that water-soluble low-molecular-weight fractions of degraded products from the wood surface were mainly derived from lignin. These degradation products contained carbonyl conjugated phenolic hydroxyl groups and had a weight-average molecular weight of about 900, as confirmed by gel permeation chromatography.

The use of singlet oxygen generators, as well as singlet oxygen quenchers, suggests that singlet oxygen participates as an effective intermediate in photooxidation reactions at the wood surface (61). 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 (53); beyond this stage, the rate of free-radical decay increases. Infrared studies revealed that carbonyl groups are generated in cellulose and lignin (62) during weathering. Water-soluble fractions of degraded wood exhibit characteristics of phenolic absorption caused by the loss of lignin. The ESCA

studies showed that oxidized wood surfaces contain higher oxygen contents than unexposed wood surfaces.

Color Changes. Light-Induced Changes. Wood exposed outdoors changes color very rapidly. Generally, the color of wood changes to yellow or brown because of the chemical breakdown (photooxidation) of lignin and wood extractives (1, 2, 7, 24, 28, 63; Figure 5). This discoloration occurs after several months of exposure in sunny, warm climates. Woods rich in extractives may become bleached before browning is visible. In the early stages of weathering, dark woods tend to become light and light woods, dark. Eventually, all woods become gray if fully exposed to sun and rain.

Changes in brightness and color were readily observed in wood exposed outdoors or to artificial UV light for a relatively short period (2, 60). Some wood species, such as redwood, southern yellow pine, and Douglas-fir, lost significant brightness in the first month of exposure. These wood species, however, regained brightness after 6 months of outdoor exposure. After an additional 6 months, the brightness decreased again. Western red cedar gained in brightness for the first 6 months of outdoor exposure, then decreased in brightness after another 6 months of exposure. Besides the change in brightness, all wood species exposed outdoors changed in color from pale yellow to brown to gray after 6 months of exposure. Significant discoloration took place between 3 and 4 months of exposure.

Hon and Feist (64) exposed four hardwoods (red oak, white oak, yellow poplar, and sweet gum) to outdoor weathering and artificial UV light. Discoloration and loss of brightness were observed for all species, regardless of their exposure conditions. White oak and sweet gum changed color at a slower rate than red oak and yellow poplar.

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 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 (Figure 6). The silver-gray layer is chiefly composed of the more leach-resistant parts of the partially degraded wood cellulose. This 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—fungi action—usually predominates, particularly in the presence of moisture.

Biologically Induced Changes. All modern studies on the weathering of wood conclude that the final discoloration (graying) of wood in the presence of moisture is practically always due to growth of fungi on the wood surface (1, 2, 54, 65-69). The most frequently observed species is *Aureobasidium*

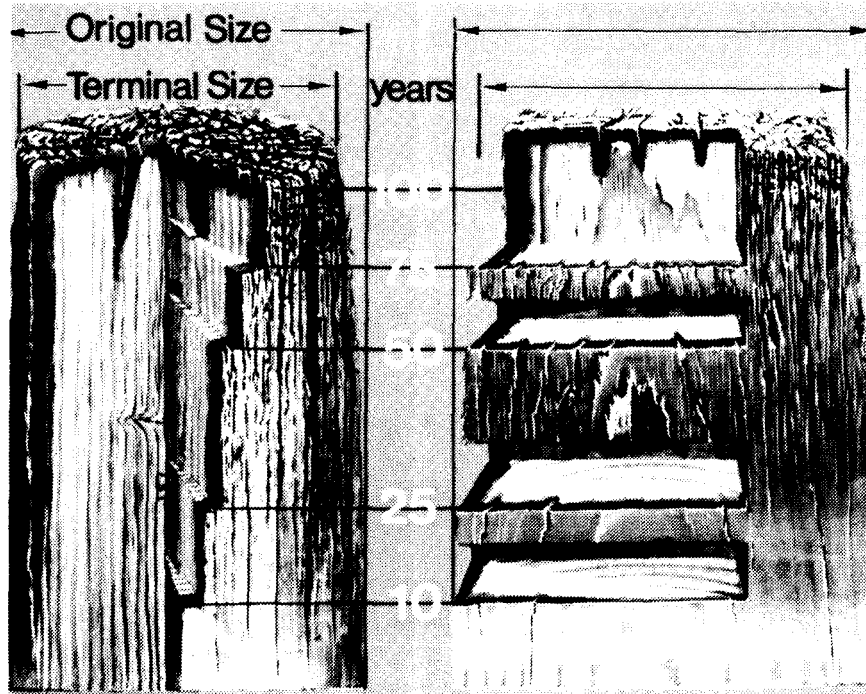


Figure 6. Artist's rendition of the weathering process of round and square timbers. Cutaway shows how wood just below the surface is relatively unchanged.

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 (70). This fungus is commonly referred to as mildew. The ecological requirements of *A. pullulans* and related fungi are modest; the most important condition for its growth is the sporadic supply of water. The fungus is otherwise relatively resistant and adaptable.

Sell (16) found that *A. pullulans* grew on finished as well as unfinished or untreated softwood and hardwood surfaces. Fungal infection resulted from wetting the wood surface with water. Sell concluded that discoloration of wood by mildew is more general than commonly believed. Sell and Leukens (54) subjected 20 European and non-European softwood and hardwood species to unprotected outdoor weathering in Switzerland; samples faced south and were inclined at 45°. Although the density and mechanical strength properties of each species were very different at the beginning of the study, these differences lessened with photochemical and mechanical deterioration, as well as attack by blue-stain fungi (mildew). After only 1 year of weathering, all wood surfaces had a uniformly weathered and gray appearance.

Physical Changes. Weathering of wood surface caused by the combined action of light and water results in surface darkening and leads to formation of macroscopic-to-microscopic intercellular and intracellular cracks or checks. Cell wall bonds near the wood surface lose their strength. As weathering continues, rainwater washes out degraded portions of the wood and further erosion takes place (Figures 4 and 7). Thus, a cyclical sequence



Figure 7. Weathered surface of softwood after 15 years of exposure in Madison, WI.

of events occurs during the natural weathering process (Figure 8). Erosion and checking differ in intensity because of different types of wood tissue on the surface, and the wood surface becomes increasingly uneven (Figure 6).

Loss of surface wood fibers caused by weathering varies according to climate and species. Browne (71) reported that the weathering process is so slow that "only 0.25 inch (6.4 mm) of thickness is lost in a centun." This would represent thickness loss for a "typical" softwood like southern pine

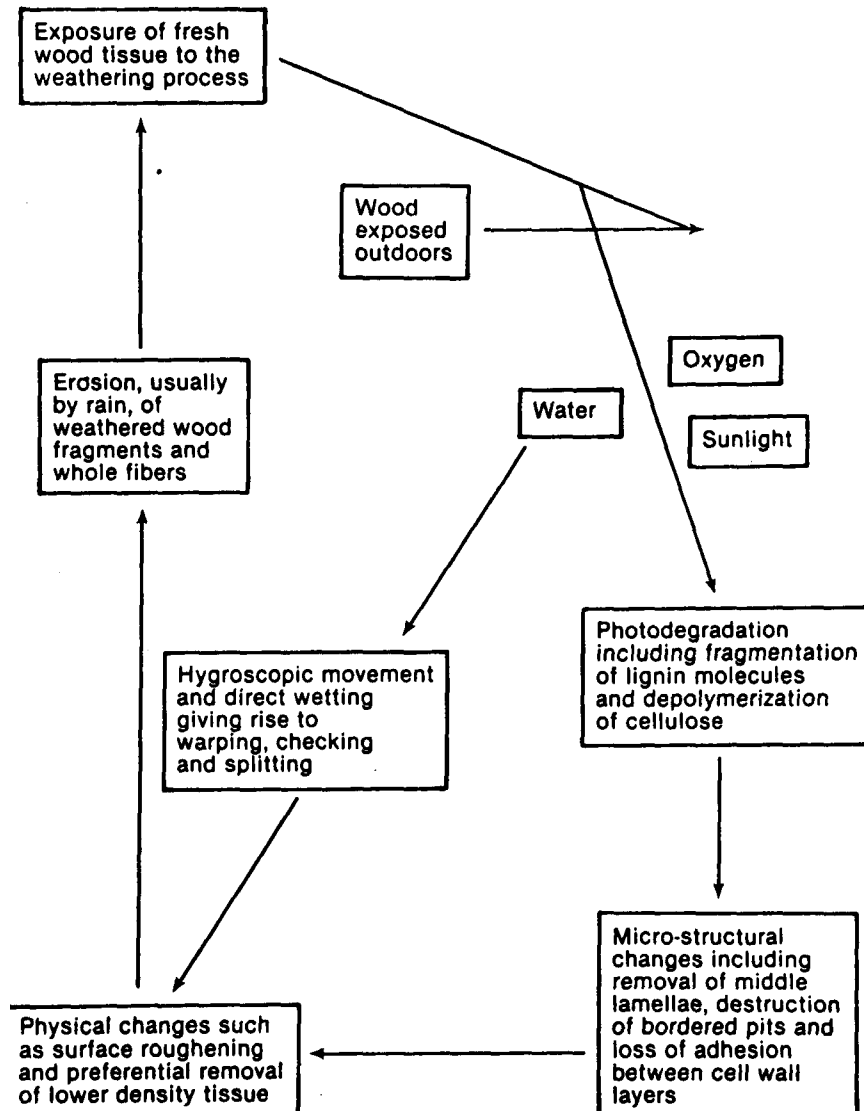


Figure 8. Cyclical sequence of events during natural weathering (Reproduced with permission from ref 88. Copyright 1986).

or Douglas-fir. Loss of surface fibers of only 1 mm per century has been reported for wood exposed in northern climates (68). In contrast, Feist and Mraz (72) reported an erosion value of 13 mm per century for western redcedar. This value was based on exposure data for 8 years of outdoor weathering at 90° facing south. Erosion data obtained from controlled accelerated weathering of redwood, Douglas-fir, Engelnmann spruce, and ponderosa pine, which were used to estimate outdoor weathering, showed that these species would erode at a rate of approximately 6 mm per 100 years, a rate similar to Browne's (71). In Norway, the 10-mm-thick cladding (siding) on stave churches was estimated to have been reduced by half over a few hundred years of weathering (73). Jemison (74) found that ponderosa pine dowels of 5-mm diameter lost 7.8% of their weight after 10 years of exposure in full sunlight, while dowels of 13-mm diameter lost 16.4%. In another study, heartwood samples of western redcedar, redwood, iroko, and teak, weathered for 3 years, lost up to 10% of their weight (75). Boettcher (76) found that the surface profile had an insignificant effect on the erosion of wood.

In some recent work at Forest products Laboratory, the erosion rate of wood exposed outdoors was estimated from data obtained by controlled accelerated weathering of several woods, by using techniques described elsewhere (72). Specimens were exposed to a high-density xenon arc light in an accelerated weathering chamber. Exposure consisted of cycles of 24 h of light, including 4 h of distilled water spray. Erosion was measured microscopically. The results showed that the hard, dense hardwoods erode at a rate similar to that observed for the latewood of softwood species (estimated at 3 mm per century, compared to 6 mm for earlywood of softwoods). Generally, the higher the density, the slower the erosion rate. Lower-density woods such as basswood erode at a faster rate than woods such as oaks, but at a slower rate than the earlywood of softwoods. The results of these studies and several others are summarized in Table IV.

In related work on the relationship of wood density to weathering rate, Sell and Feist (77) investigated the artificial weathering of 12 hardwoods and 6 softwoods. The surface erosion rate was measured with a light microscope at exposure intervals of 600 h. The results showed that the erosion rate per unit, time depended predominantly on the wood density and thus on the wood cell wall thickness. The relationship was approximately linear within a wood density range of 0.3–1.0 g/cm³.

Thus, the physical changes that occur in weathering can have a pronounced effect on the appearance of wood. From a historic viewpoint, unfinished (unprotected) wood could survive many centuries. However, the wood surface slowly wears away (erodes), and this can necessitate eventual replacement. The more severe the exposure, the faster the weathering process. The weathering process can be greatly reduced or stopped by using suitable treatments and finishes (see Protection Against Weathering). Many

Table IV. Oven-Dried Density and Erosion Rates for Different Wood Species

Wood Species	Wood Density, ^a g/cm ³	Erosion Rate, ^b μm/h
Softwoods ^c		
Douglas-fir		
Heartwood	0.53	
Earlywood	0.30	0.163
Latewood	0.95	0.040
Sapwood	0.39	
Earlywood	–	0.192
Latewood	–	0.056
Redwood		
Heartwood	0.35	
Earlywood	0.30	0.217
Latewood	0.95	0.040
Sapwood	0.32	
Earlywood	–	0.271
Latewood	–	0.063
Southern Pine		
Sapwood	0.65	
Earlywood	0.30	0.204
Latewood	0.95	0.046
Spruce, European		
Heartwood	0.41	
Earlywood	0.30	0.181
Latewood	0.95	0.042
Western redcedar		
Heartwood	0.33	
Earlywood	(0.25)	0.263
Latewood	(0.95)	0.063
Sapwood	0.27	
Earlywood	–	0.273
Latewood	–	0.139
Hardwoods ^c		
Alder, red	0.44	0.135
Ash, white	0.76	0.083
Basswood	0.41	0.160
Beech, European	0.74	0.067
Birch, yellow	0.65	0.125
Elm, American	0.53	0.090
Cherry, black	0.60	0.083
Hickory	0.81	0.060
Maple, hard	0.59	0.102
Maple, soft	0.45	0.104
Oak, red	0.67	0.083
Oak, white	0.78	0.075
Yellow-poplar	0.52	0.129

^aEarlywood and latewood densities for softwood are from the literature. Values for western redcedar are estimates.

^bErosion rate after 2400 h of accelerated weathering.

^cBecause of fairly small differences in the erosion of earlywood and latewood of the hardwoods, only one average value was measured.

treatments and finishes currently available for wood are acceptable from a historic viewpoint and will not change the general appearance of the wood.

Microscopic Changes. Microscopic changes accompany the gross physical change of wood during weathering. In a series of papers, Miniutti (78-82) reported changes in softwood surfaces after outdoor exposure. The first sign of deterioration was enlargement of apertures of bordered pits in radial walls of earlywood tracheids. Next, microchecks occurred. Miniutti showed that these microchecks 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.

Borgin (73, 83, 84) and Borgin et al. (85) used the scanning electron microscope (SEM) to study the breakdown of wood structure caused by weathering. 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 found to be remarkably stable and durable. The most stable part of the whole fiber seemed to be the microfibril. Various layers of the cell wall fail because of loss of cohesive structure between microfibrils and loss of adhesion between layers. All apertures or voids were enlarged, weakening 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 (85). Thus, as long as the main reinforcing structural elements, the microfibrils, remain intact, the major properties of wood do not undergo drastic changes.

Several publications (58, 79, 81) describe microscopic changes caused by artificial weathering (UV irradiation) of wood surfaces that resemble the changes caused by natural weathering. Coupe and Watson (14) observed longitudinal checks between adjacent walls of neighboring elements, which apparently occurred in or close to the middle lamella; longitudinal checks in element walls; and diagonal checks through pits, which probably followed the fibril angle of the S_2 layer. The SEM studies by Chang et al. (62) showed that most cell walls on exposed transverse surfaces are separated at the middle lamella region, apparently because of the degradation of lignin. However, tangential surfaces were quite resistant to UV light, compared to transverse and radial surfaces. Only microchecks were observed at the tangential cell walls.

Bamber (86) and Bamber and Summerville (87) studied the pattern of breakdown of surface wood cells and cells adjacent to the surface in radiata pine sapwood exposed outdoors for 4.5 years. The pattern was characterized by a progressive decrease in deterioration of wood cells away from the

exposed surface. Deterioration was found only 10–12 cells away 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 appeared to be lost first.

Using SEM, Groves and Banana (88) investigated the effect of natural weathering on the microstructure of radiata pine. The study suggested that under the weather conditions prevailing in Canberra, Australia, deterioration of the exposed surfaces was readily apparent after only 4 months. Complete surface degradation and erosion of some tissue were observed after only 6 months. One of the more conspicuous effects of exposure was destruction of the bordered pits. The observed changes included the following:

1. Degradation of the pit membranes.
2. Gradual enlargement of the pit aperture to the approximate limit of the pit chamber.
3. Development of microchecks in the pit borders.
4. Initial destruction of pit borders on the weather side, leaving a half-bordered structure.

The bordered pits in earlywood tracheids were completely destroyed in about 6 months. After 6 months of exposure, virtually all my tissue had disappeared from the surfaces of weathered wood and only cavities remained.

Kucera and Sell (89) studied the erosion of the large rays in European beech in tangential surfaces exposed to natural weathering. The authors observed a differential shrinkage of the ray compared to normal wood tissue, partially combined with the photochemical degradation of the wood substance. Kucera and Sell concluded that surface finishes for woods like beech would be particularly stressed around the ray area. Thus, finishes for hardwoods (with low dimensional stability and large rays) must protect the wood surface against photochemical degradation and intense moisture changes by means of adequate pigmentation and sufficient coating thickness. Consequently, finishing considerations for hardwoods are more important than those considered necessary for most softwoods.

Hon and Feist (64) investigated the erosion of several hardwood surfaces. The SEM studies showed that all wood species exhibited surface deterioration after only 30 days exposure to sunlight or 500 h to UV light. Loss of the middle lamella, separation of procumbent cells, and damage of pit structures were observed on transverse sections for all species. The ESCA studies revealed high oxygen content at the wood surfaces, indicating severe oxidation of wood exposed either outdoors or to artificial UV light. The generation of new chromophoric groups, such as conjugated carbonyls, carboxylic acids, and quinones, and the loss of lignin at the oxidized surfaces were demonstrated by infrared spectroscopy.

Many aspects of wood weathering are not completely understood. A complete understanding of the mechanisms involved in outdoor weathering would aid in developing new pretreatment and finishes to enhance wood durability. The ever-changing commercial wood supply and the introduction of previously unused species at increasing frequency pose particular challenges to the use of modern wood finishes. A detailed study of the various interactions that affect the performance of wood materials is needed to protect wood products when they are used outdoors.

Protection Against Weathering

Paint and other coatings (finishes) for wood used indoors can protect the wood for many decades and can obviate refinishing (4, 90, 91). Indoor finishes are relatively unaffected by wood properties. Outdoors, some wood finishes may last only 1–2 years because of degradation from UV light and water. The durability of outdoor finishes primarily depends 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 diseased wood (92). Other contributing factors are the nature and quality of the finish used, application techniques, pretreatment, time between refinishing, extent to which the surfaces are sheltered from the weather, and climatic and local weather conditions (93–99). The stressing factors, which influence factors and weathering effects that contribute to wood-finish performance, are summarized in Figure 9.

The primary function of any outdoor wood finish is to protect the wood surface from weathering elements (sunlight and water) and help maintain appearance (2, 4). 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 (Figures 1 and 2) (1, 2, 4, 70). Different finishes give varying degrees of protection from the weather (4, 93, 94). Generally, the greater the pigment concentration (that is, the greater the opacity), the greater the protection; paints give the most protection, transparent varnishes the least.

Any protection that surface treatments provide against light and water will be affected by the weather resistance of the bonding agents of the finish (such as drying oils, synthetic resins, and latexes) (99). These bonding agents are subject to photodegradation to some degree. The mechanism of failure of paints and other finishes has been described (90, 91, 100), and it will not be discussed further here. Wood exposed outdoors is protected from the effects of weather by various finishes, construction practices, and design factors, which have all been addressed in detail (4, 16, 93, 94, 101–104).

Two basic types of finishes (or treatments) are used to protect wood surfaces during outdoor weathering: (1) those that form a film, layer, or

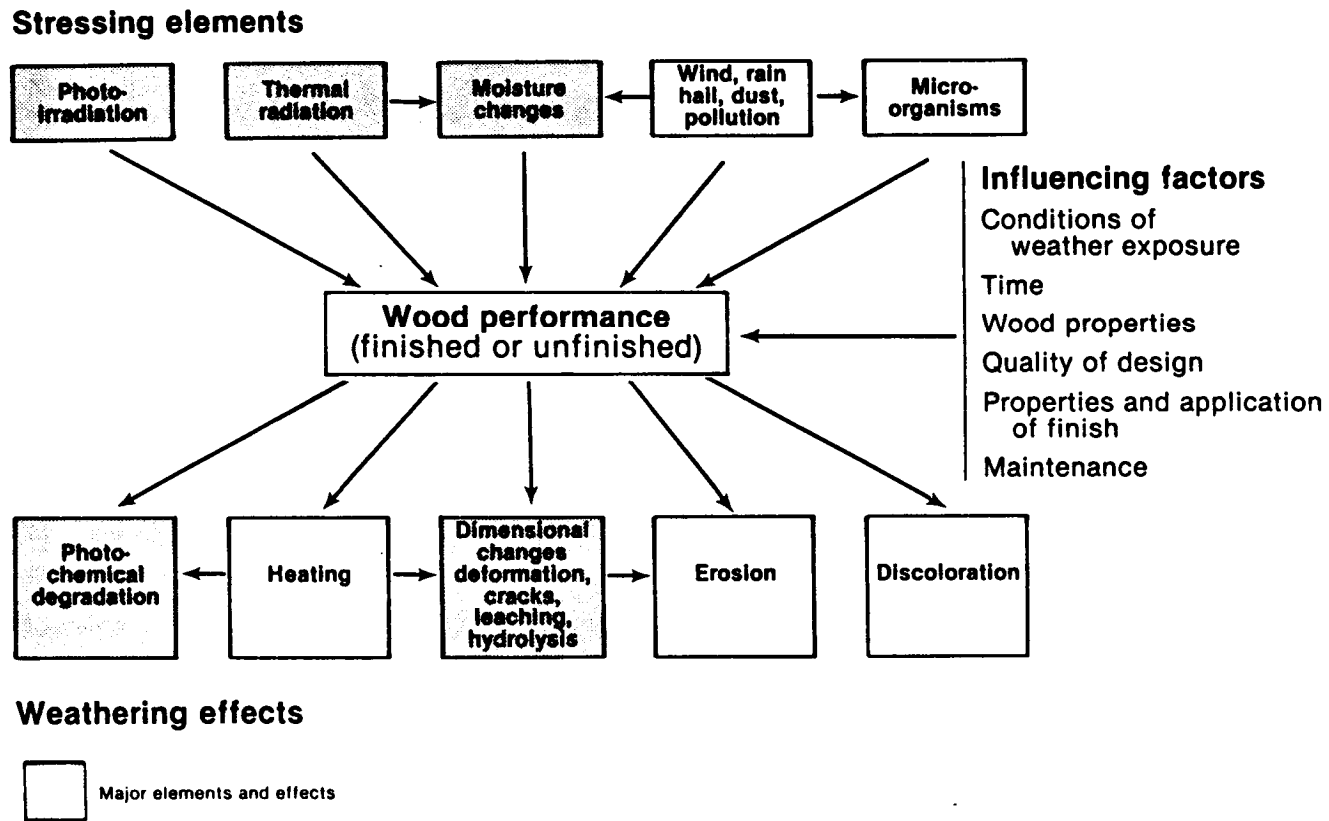


Figure 9. Stressing factors, influencing factors, and weathering effects that contribute to wood-finish performance.

coating on the wood surface (film-forming), and (2) those that penetrate the wood surface and leave no distinct layer or coating (non-film-forming).

Film-Forming Finishes. Film-forming finishes include paints of all description, varnishes, and solid-color stains, as well as overlays bonded to the wood surface.

Paints. Film-forming finishes such as paint have long been used to protect wood surfaces. Of all the finishes, paints offer the greatest degree of protection against erosion by weathering and the widest selection of colors. A nonporous paint film retards penetration of moisture and thereby reduces paint discoloration by wood extractives, paint peeling and checking, and warping of the wood (4, 98, 99). Proper pigments will essentially eliminate photodegradation of the wood surface. However, paint 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, moisture, and type of paint.

Paints are commonly divided into oil-based or solventborne systems and latex or waterborne systems (90, 105). Oil-based (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 using clear varnishes, lacquers, or shellac. Other treatments either change wood color or completely cover the wood. 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 coats are necessary for reasonable performance. Moreover, the varnish sulfate must be refinished as soon as signs of breakdown occur. In severe exposures, this may be as soon as 1 year after application. Lacquers and shellacs are usually not suitable as exterior clear finishes for wood because they are sensitive to water and crack or check easily.

The addition of colorless UV light absorbers to clear finishes sometimes helps to retain the natural color and original surface structure of wood (1, 2, 25, 106–110). Opaque pigments in paints and stains generally provide the most effective and long-lasting protection against light (55, 111–113). Even when relatively durable, clear, synthetic resin varnishes are used, the weatherproof qualities of the wood–varnish system are still limited because UV light penetrates the transparent varnish film and gradually degrades the wood underneath (29, 114, 115). Eventually, the varnish begins to flake and crack off, taking with it fibers of the wood that have been degraded photochemically (68, 79, 116).

Ashton (117, 118) reported on studies for predicting the durability of clear finishes for wood from the basic properties of the finishes. He reviewed the relationships between composition, water absorption, water vapor permeability, tensile strength, and elongation. Single and multiple regressions were used to establish the relative importance of the different properties in determining the durability of the finishes on wood exposed outdoors. The durability of clear phenolics and alkyds could be predicted from water absorption and permeability properties. Tensile strength and mechanical properties were of less importance.

Solid-Color Stains. Solid-color stains are opaque finishes (also called hiding, heavy-bodied, and opaque stains) that come in a wide range of colors and are made with a much higher concentration of pigment than the semi-transparent penetrating stains. As a result, solid-color stains totally obscure the natural wood color and grain. Oil-based or alkyd solid-color stains form a film much like paint, and consequently they can peel from the substrate. Latex-based solid-color stains are also available and likewise form a film. Both oil-based and latex-based solid-color stains are similar to thinned paints and can usually be applied over old paint or semitransparent stains.

Penetrating Finishes. Penetrating finishes, which do not form a film over the wood, include oils, water repellents, stains, preservatives, and surface treatments.

Oils. A number of oils (linseed, tung, oiticica) and modified oils have traditionally been used as penetrating wood finishes. These oils do not leave a film, and they do not last longer than 1–1.5 years because of their low resistance to UV light and water. Therefore, penetrating oils find limited use as outdoor finishes, but they are widely used as interior furniture finishes.

Water Repellents. A large proportion of the damage of exterior woodwork (such as paint defects, deformations, decay, and leakage) is a direct result of moisture changes in the wood and subsequent dimensional instability (4, 16, 99, 119–125). Water generally enters wood through open cracks, unprotected end-grain surfaces, and defects in treated surfaces. Although such problems can be avoided or at least reduced by proper design and correct choice of materials, it is extremely difficult to eliminate checks or cracks when woodwork is subjected to harsh long-term exposure. Even a high-quality coating often loses its protective ability because the coating cannot tolerate the stresses and strains of wood shrinkage and swelling, especially around joints. Eventually, the coating gives way.

Because of these problems, researchers have often suggested that woodwork exposed outdoors be protected with a coating that is both water repellent and resistant to decay fungi. Such treatment could be used as the finish itself or prior to the final finish. Materials developed for such purposes

are termed water-repellent preservatives (WRP). They generally comprise a resin (10-20%), solvent, wax (as the water repellent), and preservative (fungicide or mildewcide) (4, 16, 99, 120-122, 126).

A great store of information has been accumulated on the effectiveness of WRPS in protecting exterior wood (1, 2, 4, 112, 119-123, 127-131). The treatments can be applied by immersion (which is preferred), by brush, or by spray application. They improve the performance of many finishes and greatly add to the durability of exposed wood. Even chipboard or particleboard, which is very susceptible to moisture, can be protected against the effects of outdoor exposure by using a WRP pretreatment followed by a diffusion-resistant coating (128, 132-135).

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. The WRP reduces water damage to the wood and helps protect applied paint from the blistering, peeling, and cracking that often occur when excessive water penetrates wood.

The preservative in a WRP helps control decay and acts as a mildewcide—it kills any sulfate mildew living on the wood. Some research studies indicate that in many situations where there is a medium-to-low risk of decay, the preservative may not be needed for successful performance of the water repellent (124, 126). These studies support the general concept that protecting exposed wood from water is of prime importance in improving the durability of the wood (119).

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, semitransparent, penetrating stain (1, 2, 4, 112, 136). The pigment provides color and greatly increases the durability of the finish because UV light is partially blocked. These semitransparent stains permit much wood grain to show through; they penetrate the wood to some extent 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. The performance of stains during outdoor exposure has received a great deal of attention (137-143).

Penetrating stains are suitable for both smooth and rough surfaces. However, their performance is markedly improved if applied to roughsawn, weathered, or rough-textured wood (4, 96, 99, 112, 136, 137, 141-144) 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 solventborne resin systems and latex systems; however, waterborne (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.

Preservatives. Although not generally classified as wood finishes, preservatives do protect wood against weathering and decay, and much preservative-treated wood is exposed without any additional finish (4). The following are the three main types of preservative (an example of each is given in parentheses) (4): preservative oils (coal-tar creosote), organic solvent solutions (pentachlorophenol), and waterborne salts (chromated copper arsenate).

Although these preservatives can be applied to wood in several ways, pressure treatment provides the greatest protection against decay. In general, the greater the preservative content of pressure-treated wood, the greater resistance to weathering and the greater surface durability. The chromium-containing preservatives also protect against UV light degradation (1, 2, 144, 145).

Surface Treatments. Recent trends in the use of wood for exterior siding have emphasized natural-type finishes that enhance the texture, grain, and inherent beauty of the wood. While several approaches have been used for developing an acceptable natural finish, inorganic surface treatments have been extensively studied (145) to improve the service life of clear exterior finishes. The studies on natural wood finishes have also involved measuring the erosion of treated and untreated wood surfaces caused by leaching and by UV irradiation in accelerated weathering. A procedure was developed for quantitatively measuring the effect of erosion, as well as the effects of wood species and composition of treating solutions on resistance of the finish to leaching and UV irradiation (145). A promising method for improving the fungal resistance, color, and permanence of acid-copper chromate treatments with resorcinol was also reported.

More recent work at the Forest Products Laboratory (138, 140, 144, 146, 147) showed that certain inorganic chemicals (especially hexavalent chromium compounds), when applied as dilute aqueous solutions to wood surfaces, provide the following benefits:

1. Retard degradation of wood surfaces by UV irradiation.
2. Improve durability of UV-light-transparent polymer coatings.
3. Improve durability of paints and stains.

4. Provide a degree of dimensional stability to wood surfaces.
5. Provide fungal resistance to wood surfaces and to coatings on the surface.
6. Serve as natural finishes for wood and obviate further treatment.
7. Fix water-soluble extractives in woods such as redwood and redcedar, and thereby minimize subsequent staining of applied latex paints.

The most successful treatments investigated were those containing chromium trioxide (chromic acid, chromic anhydride), copper chromate (mixtures of soluble copper salts and soluble chromates), or ammoniacal solutions of these chemicals. The most spectacular result—an exterior natural finish with a service life of approximately 15 years—was achieved by treating the wood surface with an inorganic UV-light absorber and coating it with a clear polymer transparent to UV light. Effective inorganic treatments were ammonium chromate, ammonium copper chromate, ammonium copper-chrome-arsenate, cupriethylene diamine, copper molybdate, and copper ferricyanide. In addition, chromate treatment improved performance of oil and latex stains, linseed oil-based paint, clear latex coatings, and oil-based varnishes. Chromium treatments were found effective on both softwoods and hardwoods (103). Additional studies showed the value of using simple chromium compounds like chromium trioxide (144) and trivalent chromium compounds (148) as treatments and natural finishes.

Desai and Clarke (149) reported successful results using zinc-containing compounds. Sell et al. (150, 151) described surface treatment with chromium-copper-boron salts. Field weathering tests, leaching tests, and electron-probe microanalysis showed that this treatment was resistant to leaching and weathering. Water-soluble extractives in redwood and redcedar were fixed by treating the wood surface with dilute solutions of copper and chromium salts. This treatment permits direct application of latex paints to these woods (146).

A serious disadvantage of the chromium treatments is the toxicity of the chemicals. However, the Cr^{6+} valence state is apparently the hazardous form of chromium-containing compounds; reduction of Cr^{6+} to the lower, less hazardous trivalent state (Cr^{3+}) might make these compounds attractive as treatments for wood sulfates. Investigations (144, 147) were conducted on the fixation and interaction on wood surfaces of compounds containing hexavalent chromium. Almost total fixation of Cr^{6+} was achieved by heating wood surfaces, treated with chromium trioxide (CrO_3) solutions, for 10 min at 135 °C. Only traces of chromium of any valence state were detected in water extracts. These studies also showed that the degree of protection provided to the wood surface by CrO_3 solutions (chromic acid) is directly

related to Cr^{6+} concentration. Solution pH was important; a 4.8% CrO_3 solution was most effective at its original pH of 0.5. Surface treatment with CrO_3 reduced dimensional changes in wood exposed to water.

Liquid water uptake of CrO_3 -treated wood was decreased to that observed after treatment of wood with a water repellent. This decrease in liquid water uptake was found for treated flat-grained and vertical-grained surfaces, but not for end-grain wood, a result indicating that capillary uptake could still occur. Water repellency was observed in both water-immersion and water-spray experiments. Preliminary studies on CrO_3 -treated wood surfaces using ESCA showed that Cr^{6+} was reduced to Cr^{3+} at concentrations of 1.25% chromium. The reduction undoubtedly plays a role in the fixation of Cr^{6+} on the wood surface.

Chang et al. (62) showed that when wood was treated with 0.1940 CrO_3 solution, protective effects could be recognized on transverse surfaces even after 500 h of UV irradiation. Although some longitudinal microditches in the middle lamella zone were observed, cell walls were less deteriorated and microditches were narrower than those of untreated wood. The degree of protection was directly proportional to the concentration of CrO_3 used in the treatment. When woods were treated with 5 and 10% CrO_3 solution, most cell walls were protected. 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. The middle lamella region was mostly preserved.

The SEM studies by Chang et al. (62) revealed that both CrO_3 and ferric chloride treatments are capable of protecting wood surfaces against UV light degradation. The exact mechanism of the protection is not clearly understood. The authors speculated that the incorporation of inorganic cations at the wood surface results in the formation of a wood-cation complex that could interfere with the photochemical reaction by either emitting effective light energy or shifting the absorbing zone to a short wavelength zone to minimize light absorption. It is possible that inorganic salts would decompose peroxide intermediates, and thus prevent oxidative chain reactions at wood surfaces.

In related work, Williams and Feist (148) showed that a trivalent chromium compound was capable of adhering to wood to produce nearly the same weathering protection and water repellency as hexavalent chromium compounds. The critical factor was the ability of the chromium to fix or become unreachable, not the oxidative action of the hexavalent chromium ion on the wood. A further study by Williams and Feist (152) proved that CrO_3 fixes to both wood and pure cellulose. With both materials, complete fixation of chromium resulted in a highly water-repellent surface. The similarity between treated wood and treated cellulose indicated that chromium-cellulose interactions should be included in defining the mechanism for wood surfaces stabilized with Cr^{6+} and that previously proposed chro-

mium-wood mechanisms based solely on extractives, lignin, or hemicellulose were too limited. The authors used ESCA to evaluate wood and cellulose surfaces that had been modified by aqueous CrO_3 treatment. The data showed that Cr^{6+} was reduced to Cr^{3+} on all substrates by at least 80%. Leaching experiments confirmed this reduction to a highly water-insoluble or "fixed" chromium complex on both wood and 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 Cr^{6+} stabilization of wood surfaces described earlier.

The coating durability of organo-lead-treated southern pine in exterior exposure was reported by Barnes (153). The durability of a vinyl-acrylic latex and an alkyd paint on treated wood significantly improved. This result appeared to be independent of the type or concentration of the organo-lead-treating compounds.

Pizzi and coworkers (154-156) described in detail the role of chromium in the treatment of wood, including wood waterproofing, lignin cross-linking, kinetics of reaction, and kinetic behavior.

Hon et al. (158) showed that wood surfaces could be protected against photoinduced oxidative degradation by using effective coating agents. Several penetrating chemical agents, such as triol-G 400, polyethylene glycol (PEG-400), and 1-octadecanol, provided good protection for wood surfaces against discoloration during UV irradiation. In addition, wood surfaces coated with clear film-forming finishes, such as homo- and copolymers of 2-hydroxy-4-(3-methacryloxy-2-hydroxypropoxy)benzophenone, were extremely successful in inhibiting discoloration and surface deterioration. The infrared and UV light absorption spectra and SEM studies revealed that the clear polymeric coatings containing an internal UV-light absorber were very stable and resistant to photooxidation.

Overview of Weathering and Implications for Preserving Historic Structures

Wood exposed outdoors without protection undergoes photodegradation by UV light; leaching, hydrolysis, and swelling by water; and discoloration by staining microorganisms. Unfinished wood surfaces exposed to weather change color quickly, are roughened by photodegradation and surface checking, and erode. Although weathering causes physical as well as chemical changes, these changes affect only the surface of the exposed wood. Ultraviolet light cannot penetrate wood surfaces deeper than 75 μm , and visible light no deeper than 200 μm . This means weathering is a true surface phenomenon. Scanning electron microscopy studies show that most cell walls on exposed transverse surfaces are separated at the middle lamella region.

Half-bordered and bordered pits on exposed radial surfaces are severely degraded by UV light.

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 light absorption studies on the behavior of generated free radicals and their interactions with oxygen molecules to form hydroperoxides have revealed that free radicals and singlet oxygen play important roles in discoloration and deterioration reactions of wood surfaces.

Fortunately, wood exposed to the weather can be protected by paints, stains, and similar materials. Paints provide the most protection 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. Treatments applied to the wood before finishing, such as water-repellent preservatives and certain inorganic chemicals (chromium compounds), can significantly improve the performance of the finishes.

Many aspects of wood weathering are not completely understood. A complete understanding of the mechanisms involved in outdoor weathering would allow the development of new treatments and finishes that would greatly enhance wood durability and provide greater protection against degradation. New techniques and tools for the study of wood surfaces, such as Fourier transform infrared spectroscopy, electron spectroscopy for chemical analysis, and electron spin resonance spectroscopy, can provide a great deal of insight into the weathering process for both finished and unfinished wood. These techniques allow in-depth study of treatment and wood surface interactions and the importance of these interactions in the ultimate performance of the wood. Understanding the role of new techniques in controlling the outdoor weathering process is significant to the future use and protection of both new and historic wood exposed outdoors.

From a historic perspective, it is very important to recognize the effects of weathering. Weathering may be so severe that the wood may need to be replaced. Different finishes and treatments protect outdoor wood surfaces to varying degrees. Generally, the more the pigment, the greater the degree of protection; transparent finishes give the least protection and opaque paints the most; the effectiveness of semitransparent finishes falls in between these. Probably the most difficult aspect of wood protection is to retain the original color of the wood. This aspect may be desirable from the perspective of historic authenticity. However, constant care will be needed to protect the wood surface from the weathering elements and prevent unwanted color change. Lastly, historic authenticity requires the use of traditional finishes, even though they may not provide the most protection for the wood. The shortcomings of some traditional finishes must be taken into account when the finishes are specified for use on historic wood structures.

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