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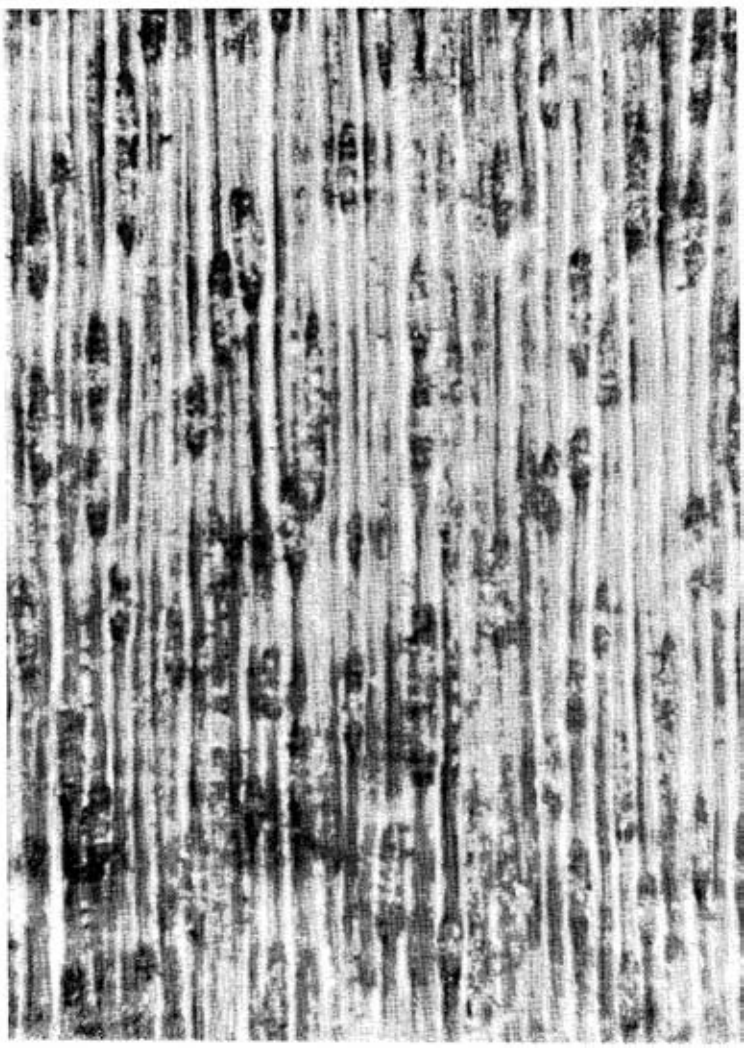
SURFACE CHARACTERISTICS OF WOOD AS THEY AFFECT DURABILITY OF FINISHES



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ABSTRACT

This report considers the behavior of wood surfaces in exterior exposures with the object of improving the durability of clear finishes applied over them Surface stabilization of wood was examined as a means for reducing strains to the covering film that are caused by movement of the wood substrate as humidity conditions change. Improved performance of a polyurethane and a polyacrylate emulsion finish were observed on wood surfaces that had been given various degrees of stabilization with a phenolic resin. The effect of light on wood was also studied. Exposure of wood to ultraviolet light caused the formation of volatile products of degradation, Changes in the chemical properties of the wood were also noted. The rate of formation of the volatile products was useful in evaluating the effectiveness of treatments designed to protect wood from degradation by light.

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SURFACE CHARACTERISTICS OF WOOD AS THEY AFFECT DURABILITY OF FINISHES

BY

Forest Products Laboratory [1] Forest Service
U. S. Department of Agriculture

INTRODUCTION

This research program was undertaken with the broad objective of improving the performance of exterior finishes on wood. Basic to such improved performance is an understanding of the actual behavior of both the wood and the protecting finish at the area of contact between the two under the severe conditions which occur in service. With a better knowledge of the mechanisms Leading to the failures of finish coatings, the way is opened to the development of improved finishes. improved wood substrates or both.

This area of research has, of course, been under study by many investigators for some time. The present. study was sponsored by the following three agencies with a common goal and all research was carried on at the Forest Products Laboratory:

[2]National Forest Products Association
1619 Massachusetts Avenue, N.W.
Washington, D.C. 20036

National Paint, Varnish, and
Lacquer Association
1500 Rhode Island Avenue, N.W.
Washington, D.C. 20005

Forest Products Laboratory
Madison, Wisconsin 53 705

Actual research began in July of 1962 with the early work consisting of library research and the preparation of study plans. A program of about 3 years duration was planned. To guide the study and to keep everyone informed, a steering committee was established consisting of representatives from both associations who met at about 6-month intervals with the scientists involved. A smaller liaison committee met at more frequent intervals.

Five progress reports have been issued since the start of the program These reports were given limited distribution to the associations directly involved. The pertinent information presented in the progress reports is now brought together in this report.

This report concludes the planned phase of this research. Evaluation of exposure samples, especially those exposed to outdoor weathering conditions will continue and will be reported from time to time. The Forest Products Laboratory will continue to pursue several promising leads uncovered in the present investigation. It is hoped that other investigations will make profitable use of the reported results through continued research

Objective

A film of paint or clear finish on wood is exposed to a number of potentially disruptive forces during outdoor weathering. Sunlight and

[1]Maintained at Madison, Wis., in cooperation with the University of Wisconsin.
[2]At the time this research was initiated, this association was the National Lumber Manufacturers' Association.

moisture may promote photodegradation of the film, continued cure and embrittlement of film photodegradation of the wood at the interface, decay of wood at the interface, differential swelling of the finish coating and immediate wood surface, and other factors. The general objective of this project was to determine the importance of these factors and to suggest possible remedies for their control. The work was divided into two general areas: (1) To study methods for stabilizing the wood surface and to determine if such stabilization would extend the life of the applied finish; (2) to study the action of ultraviolet light on the surface of wood.

Planned Research Program

Although this research was conducted by two separate research divisions of the Laboratory, liaison in planning and conducting various phases of the work was maintained by all staff members assigned to the project. This proved especially valuable in the latter stages of the work where the really close relationship between the two separate phases became apparent. Extra dividends of this research are a number of new research techniques which were developed and are presented in the report. They will be particularly useful in continuing this work.

Surface stabilization.--The Forest Products Laboratory has done considerable work on dimensional stabilization of bulk wood by chemical means, Preliminary evaluations indicated that this stabilized wood had improved paint-holding properties. Such bulk impregnation is not acceptable because of cost, but did suggest an investigation of the possibility of obtaining improved paint performance by stabilizing the wood surface only. The current research included studies of the mechanics of surface stabilization, experimentation with two arbitrarily selected stabilizing media, and two arbitrarily selected clear finishes. Various treating and finishing systems were evaluated by exposure in a weatherometer. For some studies, companion samples were also exposed to outdoor weathering.

Photodegradation.--Most contemporary exterior clear finishes for wood show signs of degradation with the first year of exposure--usually a hazy appearance in some areas which has been described as a loss of adhesion between finish and wood. In latter stages of degradation the film cracks and then peels or flakes from the surface. The degradation is retarded greatly when sunlight is restricted or when the finishes are pigmented, This study was designed to obtain information on the mechanism of failure by determining the chemical changes which occur in a wood surface and the rates at which these changes occur under exposure to ultraviolet light. The nature of the wood deterioration which occurs under exposure to ultraviolet light of various wavelengths and in various controlled atmospheres is reported,

Interpreting Results

The detailed results obtained are reported in the two separate parts of this combined report. Highly significant and of great potential is the reported improvement in performance of clear finishes on surface: modified woods. Both the surface stabilization methods and the finishing systems used were limited in this study so that a fundamental understanding of the principles could be gained. The results presented should therefore be used only as a basis for continued development.

It is unfortunate that a more exact method for measuring paint performance is not available. The investigator must rely on visual observations of specimens exposed to an arbitrary exposure cycle, The reader of a report is further handicapped by some loss of detail in the reproduction of photographic evidence. In spite of these limitations in interpreting. results, the data presented show considerable promise.

Of equal importance are the findings which help explain the degradation process of a wood surface under severe exposure to damaging light conditions. The report shows that irradiation of wood with ultraviolet light produces a number of chemical changes In the wood surface. Information on the nature of the degradation products produced during the exposure cycle and the rate at which they are produced under varying exposure conditions is presented in considerable detail. This information will be of value in developing new finishes and new finishing systems.

SURFACE CHARACTERISTICS OF WOOD
AS THEY AFFECT DURABILITY OF FINISHES

PART I. SURFACE STABILIZATION

BY

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SUMMARY

Surface stabilization of wood was evaluated as a method of improving the durability of clear finishes exposed to severe weathering conditions. Two finishes of completely different characteristics were applied to wood surfaces that had been given either short-time immersion or pressure treatment with a phenolic resin. Improvements in the polyurethane and the polyacrylate emulsion finishes were observed. The phenolic resin used may have been just as important as an absorber of ultraviolet light as it was as a dimensional stabilization treatment.

INTRODUCTION

The dimensional instability of wood is a factor responsible for the poor weathering of finishes over wood. A useful modification of wood, then, is one which reduces such instability. Earlier work (9)[1] showed that finishes laid down on Douglas-fir faced with 1/32-inch acetyl at e d Douglas-fir veneer were still sound after 8 years of outdoor weathering, However, such stabilization procedures are very cumbersome. The suggestion was made that the surface region of whole wood be treated to produce a gradient of stability. An example of such a gradient is shown in figure 1, obtained by limited face diffusion of polyethylene glycol-1000 into green wood. Note the graded bulking. The wood here swells or shrinks mainly in the untreated or nonbulked region. The gradient, however, was obtained after several days of treatment--obviously too long.

We sought to develop simple means for stabilizing a wood surface and to investigate the weathering performance of clear finishes on such surfaces. Actually, of course, stabilization will occur throughout a surface region, rather than at the immediate surface. Although the term "surface stabilization" originally referred to dimensional stabilization, it became clear, as a result of the work reported in the second phase of this study, that other types of stabilization may also be desirable.

SURFACE STABILIZATION

Surface stabilization is obtained by allowing the treating solution to penetrate into the wood for a limited time. Theoretically. diffusion of stabilizing chemical into green wood has advantages. Diffusion conditions are excellent, and the usual seasoning step can be combined with the drying step following treatment. Depth of treatment depends on the duration of exposure, with short exposures required by economic factors. Variability in absorption or depth of treatment is often encountered. This is due to variability in "greeness" and to the marked tendency of the waterborne solute to migrate to the immediate

[1] Underlined numbers in parentheses refer to Literature Cited on page 22.

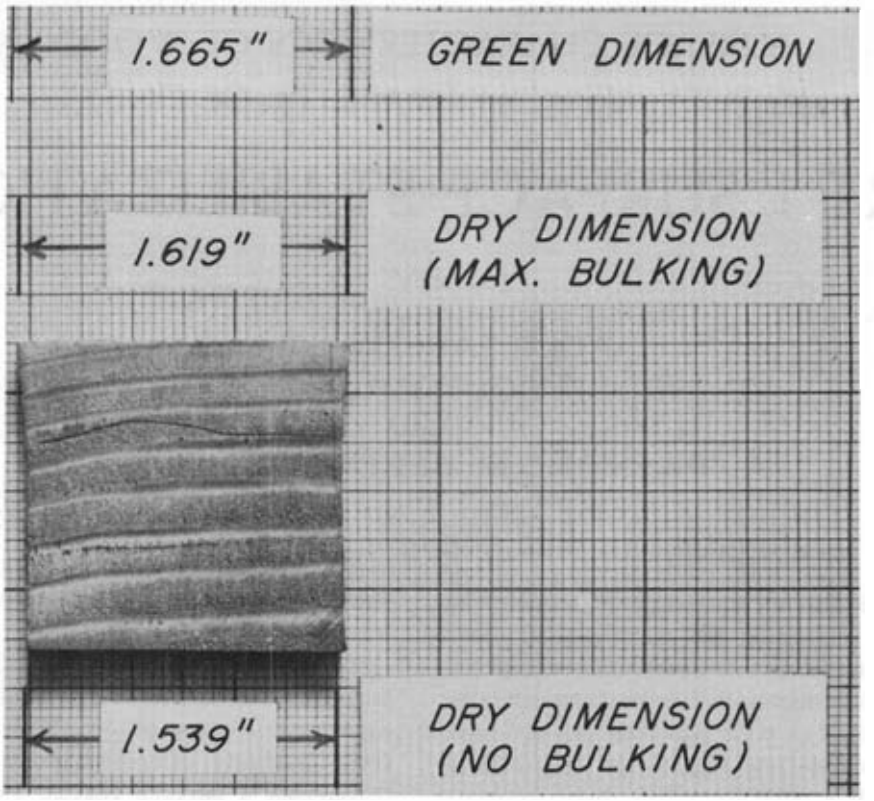

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Figure 1.--Cross section cut from a block which had been exposed only on the upper face, while green, to an aqueous solution of polyethylene glycol-1000. The block was subsequently dried to show this gradient of dimensional stability.

surface on drying excessively green wood (5). To evaluate the degree of solute penetration, experiments with 1/2-hour radial diffusion of sodium chloride from 20 percent solutions into green white fir showed that with fully waterlogged wood a concentration of 30 percent salt (dry basis) is found at a depth of 30 mils (about 25 to 30 tracheid diameters) from the surface of the green wood. With less than a fully saturated condition, the absorption is variable and considerably smaller. Similar results were found with ponderosa pine.

Air-dry wood can also be treated in which case penetration occurs by a combination of capillarity and diffusion. An excellent way to study face penetration is by means of the Cobb test. Essentially, an area of 100 square centimeters is dammed off on the test face. The liquid or solution is poured in to a depth of 1/2 centimeter. Following an arbitrary period of time, the liquid is poured off, the surface wiped, and the wood removed and weighed. Table 1 shows the absorption of a series of silicones by ponderosa pine (radially). Silicones have no stabilizing properties but were used here to show the effect of viscosity. (For reference purposes, the viscosity of water is about 0.9 centipoise.)

Penetration into heartwood is very small. The especially low value with the 0.65-centipoise silicone is not real, but due to an error associated with its high volatility. Similar low values for penetration of water into heartwood were found. If the low absorption of water by heartwood were due exclusively to poor wetting, one would expect a much higher penetration into heartwood by the silicones, whose surface tension is one-third that of water. The absence of a higher penetration means that the barrier to penetration of solutions into heartwood is due to poorly communicating cell cavities (lumina) and not to poor wetting.

Penetration into sapwood is very rapid. In 1 minute, more than three times as much silicone with a viscosity of 2 centipoises was absorbed as water with less than half the Viscosity. This suggests that with sapwood, the degree of wetting plays an important role. If true, the age of the wood surface should be important. Table 2 shows

Table 1.--Effect of silicone viscosity on face penetration by capillarity

Specimen	Absorption time	Absorption			
		0.65 centipoise	2.0 centipoises	10 centipoises	50 centipoises
	Min.	G.	G.	G.	G.
Heartwood	1	0.04	0.15	0.17	0.15
	5	.03	.20	.18	.17
	10	.07	.22	.22	.17
Sapwood	1	>5.5	>3.9	2.0	1.41
	5	>7.2	--	>4.0	1.90
	10	--	--	--	1.80

Table 2.--Effect of surface aging on face penetration with water

Age of surface	Absorption time	Absorption[1]
	Min.	G.
1 day	1	1.4
	5	3.3
	10	>5.1
1 year	1	1.1
	5	2.0
	10	2.6

[1]Average of three values.

Table 3.--Face penetration of 17 percent phenolic resin into lightly planed ponderosa pine

Sample	Absorption time	Absorption	Range[1]
	Min.	G.	G.
Heartwood	1	0.30	0.02
	5	.37	.07
	10	.46	.09
Sapwood	1	2.09	.87
	5	3.51	1.88
	10	>4.48	1.40

[1]Maximum spread within three values.

the absorption of liquid water by ponderosa pine, freshly planed or stored 1 year at 65 percent relative humidity after planing.

Obviously, surface aging has a serious effect on the short-time absorption of liquids or solutions that have a high surface tension. Herczeg (4) found the contact angle of glycerol on wood increased from about 40 to 75 degrees as the age of the surface increased from 0 to 45 hours.

Cobb tests were made with 17 percent water-soluble phenolic resin solutions (table 3). Such solutions, as described later, were used extensively for surface stabilizing wood.

The absorption by heartwood, again, is very small; that by sapwood, considerably greater, but of the same order as for water. The higher viscosity (2 centipoises) is compensated by lower surface tension (55 dynes per centimeter compared to 7 dynes per centimeter forwater). However the range in sapwood is disturbingly great, indicating variable wetting.

The uncertainties in degree of absorption by sapwood are minimized by short-time pressure treatments. No attempt was made to learn specifically, the effect of degree of absorption and depth of treatment of surface stabilizers on the subsequent weathering performance of applied clear finishes. This would have been extremely time consuming and very likely ambiguous. Instead, therefore, two stabilizing procedures were adopted:

1. Immersion of air-dry wood (end coated) in 17 percent water-soluble phenolic resin solution for 1/2 hour.
2. Pressure treatment with the same solution for 5 minutes at 75 pounds per square inch.

Following treatment, me wood was dried in a kiln to remove water and cure the resin. The kiln was maintained at 160° F. dry bulb and 150° F. Wet bulb for 1 day followed by 2 days at 180° F. dry bulb and 160° F. wet bulb. This schedule was an arbitrary one and very likely can be shortened. The use of phenolic resin does not necessarily imply that this is the ideal stabilizing agent. Many others probably exist. Phenolic resin was chosen to limit the scope of the study and to get on with the main objective: that is, to learn if such stabilization improves the weatherability of clear finishes.

SOME PROPERTIES OF SURFACE-STABILIZED WOOD

Earlier work with Douglas-fir plywood showed that with the face veneers (only) containing 12 percent phenolic resin, the number of face checks after 6 months of weathering was 90 percent less than in plywood with untreated faces. Figure 2 shows the results of 2 years of weathering of plywood faced with veneer containing 30 percent resin (9). Substantially reduced checking is obvious. The panels, however, showed marked discolorations probably because of photo-oxida-

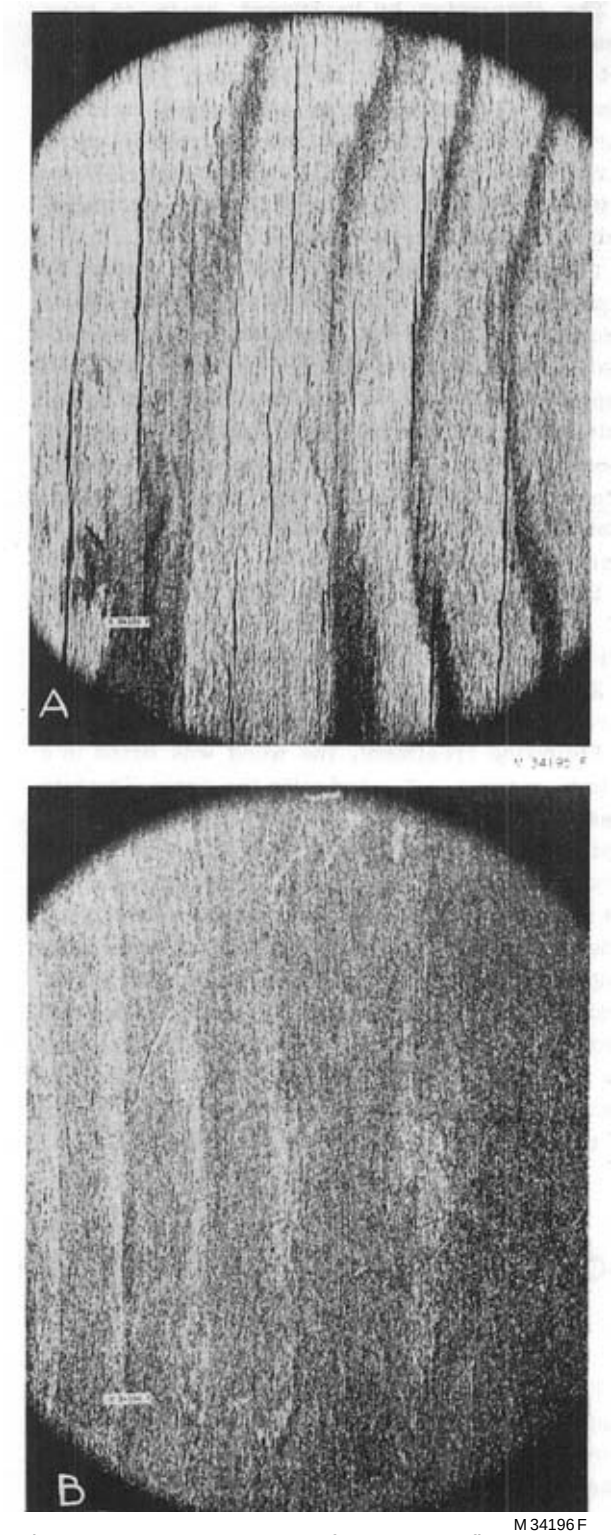

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Figure 2.--Appearance of Douglas-fir panels after 2 years of outdoor weathering.

A panel: non-stabilized face

B panel: stabilized face--30 percent phenolic resin

tion. Phenolic resins are excellent absorbers of ultraviolet light and the panels, of course, were "bathed" in air.

Ponderosa pine boards were surface stabilized with the phenolic resin solution and tested for water penetration by the Cobb test [table 4). That the stabilizing treatment was able to keep out the water is obvious, especially by pressure treatment.

Similarly treated boards were suspended in a humidity room maintained at 80° F. and 97 percent relative humidity. After 1 month, the control showed biological discoloration. The treated specimens appeared bright. Surface stabilization, therefore, should minimize soft-rot problems at wood-finish interfaces (2).

The steady state permeability coefficient of moisture in 1/16-inch-thick treated birch veneer was measured (30 to 90 percent relative humidity) (10). As shown in table 5, the treatment with 13 percent phenolic resin caused the permeability to drop by 75 percent. In other words, the moisture

Table 4.--Face penetration of water into surface-stabilized sapwood

Specimen	Absorption after--		
	1 minute	5 minutes	10 minutes
	G.	G.	G.
Control	1.4	3.3	>5.1
Stabilized by immersion	.6	1.9	>3.4
Stabilized by pressure	.3	1.2	>2.4

Table 5.--Moisture permeability through stablilzed birch veneer

Specimen	Permeability coefficient	Approximate reduction in permeability
	G./hr./cm.^{2}/mm. Hg.	Pct.
Control	1.53×10^{-5}	0
Veneer containing:		
21 percent resin	$.25 \times 10^{-5}$	85
18 percent resin	$.21 \times 10^{-5}$	85
13 percent resin	$.41 \times 10^{-5}$	75
9 percent resin	$.65 \times 10^{-5}$	60
No resin but:		
1 coat polyurethane finish	$.55 \times 10^{-5}$	65
2 coats polyurethane finish	$.13 \times 10^{-5}$	90

Figure 3.--Unstabilized ponderosa pine sapwood (13X magnification).

Figure 4.--Ponderosa pine sapwood, surface stabilized (13X magnification).

permeability of a thin surface region of wood stabilized with about 15 percent resin is only 25 percent that of a similar region having no treatment. (These are approximate, since permeabilities also depend on moisture levels (10).)

Thus, several beneficial effects are obtained by treating a wood surface with phenolic resin.

A possible adverse effect of surface stabilization was evidenced in grain raising. With ponderosa pine, it is not serious as shown in figures 3 and 4. With dense woods, grain raising may be more serious. This will be discussed later. Severe nonuniform discoloration occurs on weathering. As shown later, clear finishes can minimize this.

SELECTION OF CLEAR FINISH

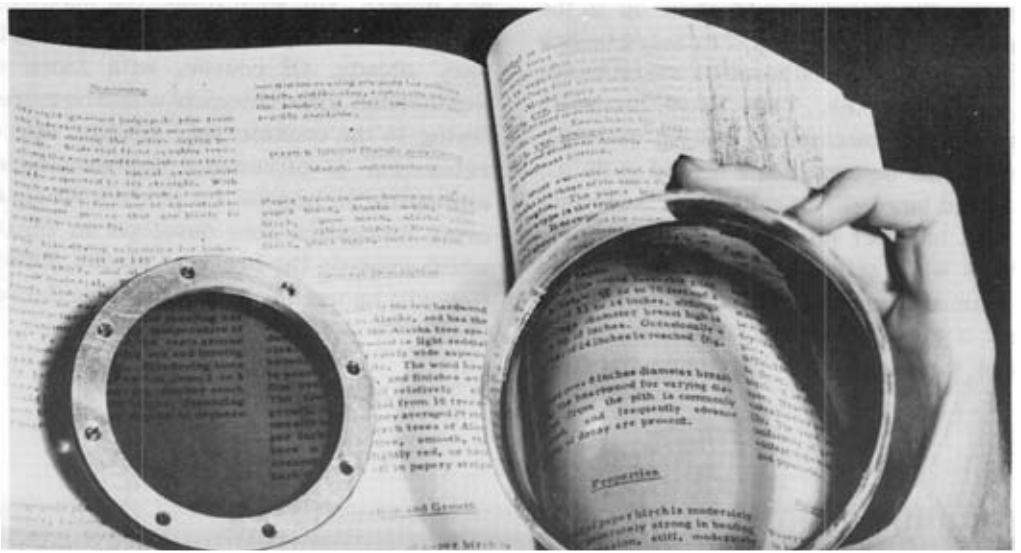
There was no desire to get involved in the "thicket" of finish comparisons. Accordingly, two distinctly different finishes were chosen.

1. Oil-Modified Polyurethane in Mineral Spirits

Film whose shrinkage during casting was restrained are shown in figure 5 (1). A 3-mil-thick flim had only 2 percent of the moisture permeability of 1/32-inch birch veneer (33 mils). Thus, when bonded to wood, the rate with which moisture gets to the underlying wood should be very small. (Provided, of course, the film remains

Figure 5.--Right: Three-mil-thick polyurethane film cast across a 5-inch glass cylinder.

Left: Similar polyurethane film exposed to ultraviolet light for 8 days. Note the change in color from the film on the right. M 126 699



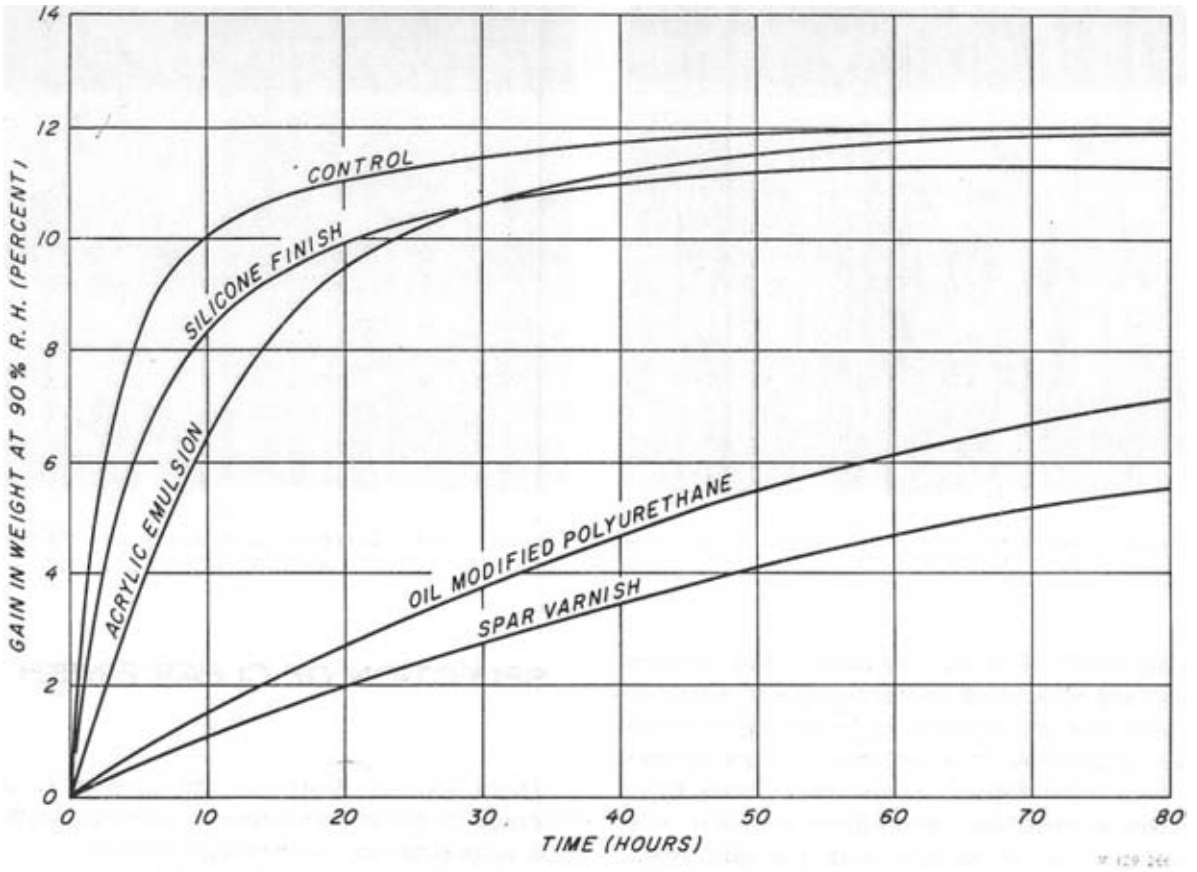


Figure 6.--Rate of gain in weight of 1/8-inch flatsawed ponderosa pine sapwood protected on both faces (and ends) with two coats of the indicated finish. Exposure was first at 30 percent relative humidity followed by a gradual increase in relative humidity to 90 percent. Other finishes are included for comparison.

intact.) This is confirmed in table 5, as well as in figure 6.

This is a plus factor. A negative factor is seen in table 6. The light absorption of films shown in figure 5 was measured with a Beckman spectrophotometer.

Considerable absorption occurs below 4000 angstroms (ultraviolet region). This should be harmful to the films and should show up in the mechanical properties. Strips, 1/2 by 3-1/2 inches were cut from films, unweathered or weathered in an Atlas weatherometer. They were tested in simple tension in a mechanical testing machine. Unweathered films or even films heated at 60° C. for 8 days could be readily strained 2 or 3 percent at a rate of 1 inch per minute without failure, These strains were selected, far it was believed that even with a 50 percent reduction in surface swelling as a result of resin treatment, under extreme use conditions the maximum swelling of a dense commercial wood could be about 2 to 3 percent. At these strains, the maximum tensile stress was about 3,500 pounds per square inch. This relaxed fairly rapidly at constant strain. Strips that had weathered 8 days in ultraviolet light were somewhat embrittled and could be strained only 2 percent, provided the strain rate was considerably smaller, for example, 0.1 inch per minute. For such film, the maximum stress was about 5,500 pounds per square inch. It relaxed very slowly. Of course, with more extensive weathering, embrittlement would be more serious. Owing to the considerably smaller rate of stress relaxation in ultraviolet light-weathered films, attempting to impose a 2 percent strain at a moderate elongation rate develops an initial stress which exceeds the breaking stress. This information will be useful in understanding the weathering of panels.

Table 6.--Percent of absorption of light by polyurethane film

Wavelength	Film thickness			
	1-1/2 mils		4-1/2 mils	
	Original	Heated at 160° F., 24 hours	Original	Heated at 160° F., 24 hours
A	Pct.	Pct.	Pct.	Pct.
4500	--	--	--	45
4000	25	28	80	100
3800	45	--	100	100
3500	85	100	100	100
3400	100	100	100	100

2. Polyacrylate Emulsion

A clear finish that differed radically from the polyurethane was sought which did not absorb ultraviolet light. Emulsions are available for paint formulations. These axe based on polymers such as butadiene-styrene, polyvinyl acetate, and polyalkyl methacrylates. Finishes based on butadiene-styrene absorb ultraviolet light so this polymer was not considered. Polyalkyl methacrylates were reputed to be ultraviolet transparent and were selected as a prototype of a clear finish. Samples of Rhoplex 34 and 73[2] were obtained at 50 percent solids level. The former, spread on wood, forms a clear, glossy film, not quite tack-free. The latter forms a hard, severely checked film. A 1:1 blend forms a tackfree, checkfree film on wood. The emulsified particles are probably not more than a micron in diameter, therefore it is doubtful whether any penetration occurred beyond the first tier of wood cells (radial or tangential direction). Ponderosa pine was given two coats of the latex and evaluated with the Cobb test for water absorption. The results are shown in table 7.

Note how effectively 34 and 34/73 films exclude liquid water.

Two coats of 34/73 acrylic emulsion were brushed onto ponderosa pine sapwood, and the rate of absorption of moisture at 90 percent relative humidity was measured (figure 6). This type of film is a much poorer water vapor barrier than polyurethane, but is an excellent liquid water barrier. The emulsions are stabilized with surface-active agents and gums. On drying, these concentrate at the latex particle interfaces and probably are responsible for the high vapor transmission rate. These interparticle layers are probably only hundreds of angstrom thick; the films, therefore appear optically homogeneous (7).

Table 7.--Face absorption of water by ponderosa pine sapwood finished with Rhoplex 34/73

Surface coating	Immersion time	Water absorption
	Min.	G.
None	1	1.36
None	3	2.10
Rhoplex 34	3	.01
Rhoplex 73	3	.92
Rhoplex 34/73 (1:1)	3	.02

Two coats were brushed onto a quartz plate, and the light absorption measured. Between 4000 and 3000 A (angatroms), less than 10 percent of incident light was absorbed, Little photo-degradation should occur. The flexibility of crude films did not seem to suffer after 8 days of continuous exposure to ultraviolet Further evaluation was made by measuring the equilibrium swelling (liquid absorption) of the films in toluene. An appreciable reduction in liquid absorption would occur if weathering caused cross linking (analogous to the appreciable reduction in swelling of rubber in toluene after vulcanization). Cast films were exposed in the weatherometer and

[2] Mention of trade names and commercial enterprises or products is solely for necessary information. No endorsement by the U.S. Department of Agriculture is implied.

Table 8.--Effect of ultraviolet radiation on the absorption of toluene by Rhoplex films

Samples	Amount of remaining after immersion in toluene	Toluene absorbed by insoluble residue
	Pct.	Pct.
Unweathered	77	1,000
3 days in weatherometer	82	730
7 days in weatherometer	75	780

immersed in toluene for 24 hours (table 8). Note that 20 to 25 percent of the material dissolved in the toluene, regardless of the degree of weathering. Although the unweathered film absorbed 10 times its weight of toluene, the 3- and 7-day weathered films absorbed about 7-1/2times their weight. Literally, this could mean some cross linking in the weathered film; however, the effect after 7 days was the same as that after 3 days. and it can be concluded that cross linking, if real, is alight.

PREPARATION AND WEATHERING OF CLEAR FINISHES ON SURFACE-STABILIZED WOOD

Commercial boards, 30 by 5 by 1-1/8 inches, were lightly dressed, end coated, and treated with phenolic resin to stabilize the surfaces. Following cure, the boards were sliced in two, giving flat 1/2-inch boards with one stabilized face. In addition, 5/8-inch boards were treated. cured, and not sliced. Here, both faces were stabilized. About 3 inches were trimmed off each end, and the boards were cut into 7-inch lengths. These were end coated and two coats of the finish applied. Most of the weathering was in an Atlas weatherometer with the following schedule: 102 minutes to carbon arc, and 18 minutes to water spray every 2 hours for 20 hours; 3 hours to water spray and 1. hour at 0° F. This constituted one cycle. These cycles were repeated for the indicated length of time.

Ponderosa Pine

This is a low-to-medium density wood, There was no evidence of serious grain raising following treatment with resin and no problem in applying the finish to the surface-stabilized wood. Commercial boards were obtained from a local supplier. The boards had a high proportion of nominal flat grain.

The panels shown in figure 7 are heartwood, finished with polyurethane and kept in the weatherometer for 12 weeks. The two top panels were surface stabilized by pressure treatment, the lower panel was not surface-stabilized. The improved performance of the finish over the surface-stabilized wood is obvious.

Considering that very little resin penetrates into heartwood (table 3) it is unlikely that true dimensional stability is imparted to the surface region of heartwood. A very thin layer of phenolic resin is probably present at the wood-finish interface adding to the vapor excluding effectiveness of the finish. Thus, during cyclic weathering the rate of entrance of moisture into the wood is extremely small. As a consequence, the strain rate imposed on the brittle polyurethane film is very small, and the film does not suffer.

Considerably more work was done with sapwood, Table 9 gives a description of some of the stabilized boards finished with polyurethane.

The panels described in table 9 are shown in figure 8, after 8 weeks in the weatherometer. The unstabilized panels (No. 2, top row) checked badly in the finish and wood. There was a masked loss of finish. Exposure in the weatherometer is severe in the sense that the backs of the panels are also wetted; yet, results similar to the No. 2 series were obtained with another unstabilized group in which the backs, too, had been coated with polyurethane. The finish and wood in the front (exposed side) were severely checked. The backs, however, were in excellent condition. The deterioration of the exposed finish was not due to ingress of moisture from the rear, but was attributed to severe film embrittlement and inability of the finish to accept moderate strains from the swelling of the underlying wood.

The diffusion-treated panels (No. 8, bottom row) show checks in the finish, but very little in the wood. Similar results were found with another group of diffusion-stabilized panels, which in addition, had two coats of polyurethane on the backs. After weathering, the finish on the backs was in excellent condition and showed no deterioration. The finish in the front became severely brittle because of direct exposure to the

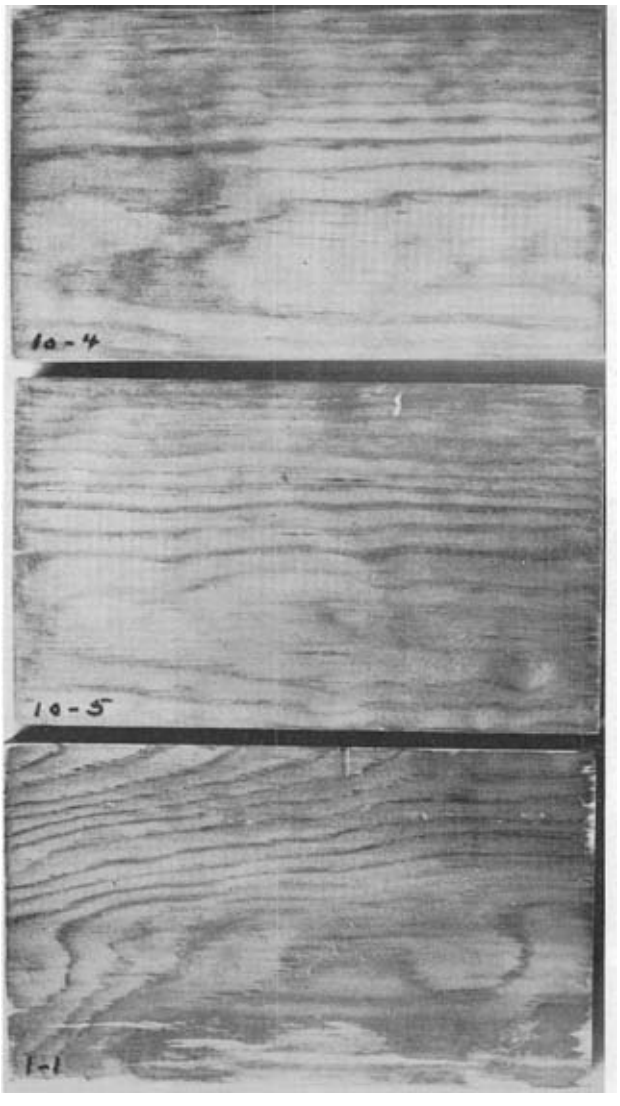


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Figure 7. --Ponderosa pi ne heartwood after 12 weeks in the weatherometer. The two upper panels (10-4 and 10-5) were surface stabilized by pressure treatment and coated with polyurethane. The lower panel (1-1). which shown some bleaching, was not surface stabilized but was coated with polyurethane.

light. Since the surface region immediately below the films was only lightly stabilized (diffusion

high enough rate to cause the brittle, overlying film to fail locally. The swelling of the wood fa not due to ingress of moisture from the rear.

The pressure-treated panels (No. 12, middle row) look excellent. There is no checking in either finish or wood. The backs were completely panels following 8 weeks in the weatherometer; that is. the panels were slightly concave towards the untreated side. A second group of pressure-treated panels which had been also brush treated with a water repellent on the back were flat.

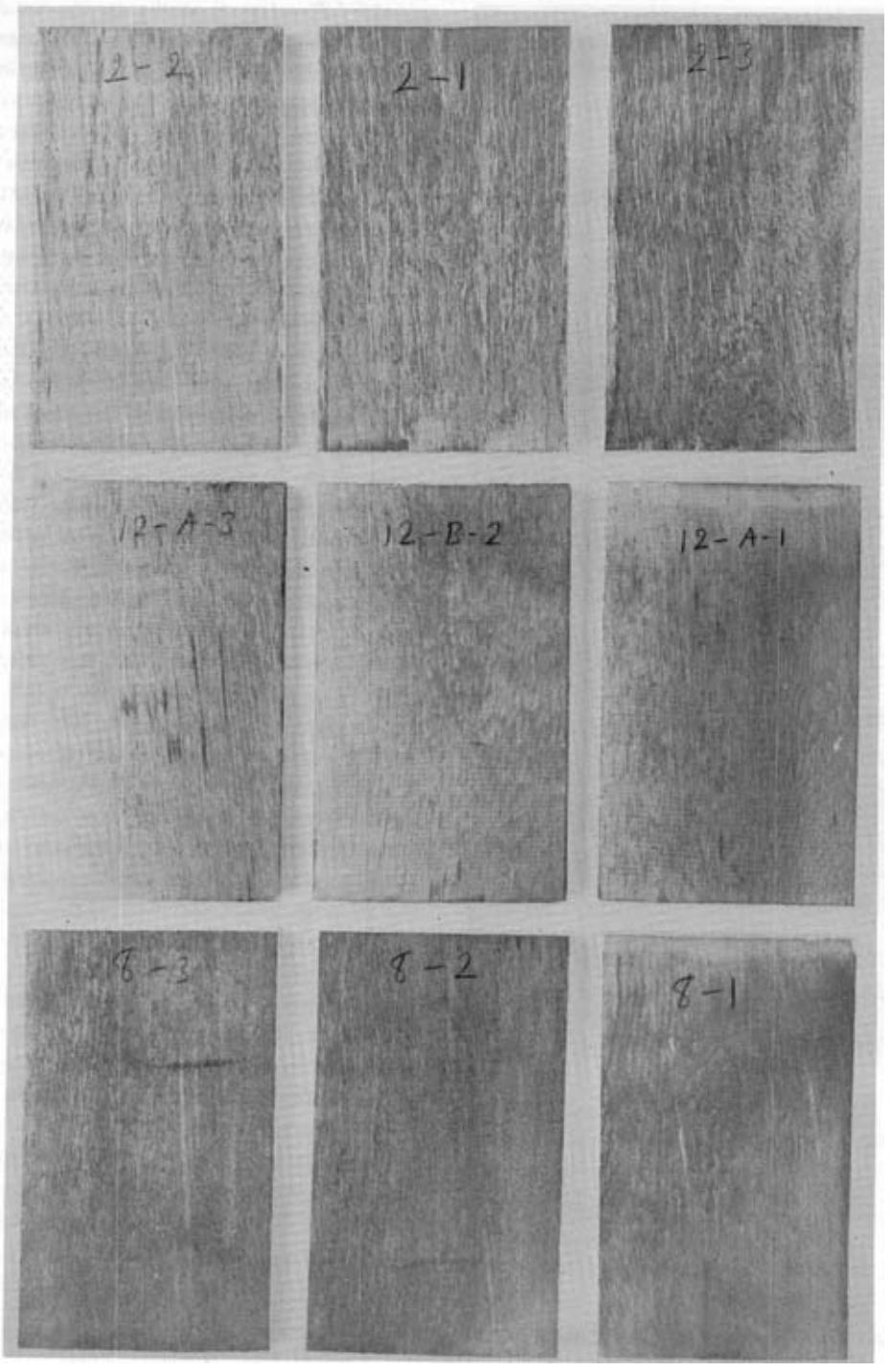
This was a particularly instructive experiment, for it tied together degree of stabilization (diffusion versus pressure), ultraviolet radiation, and back protection on the performance of the polyurethane finish. Apparently, back protection on the 5/8-inch hoards is without consequence, although in 1/2-inch boards it prevents slight cupping. Ultraviolet radiation is serious, but, deterioration of the finish does not show up if the swelling capacity and swelling rate of the under lying surface region of the wood is very small. This desirable situation occurs with wood, surface stabilized by short-time pressure treatment. Still, a disturbing feature was noted in No. 12 as well as in the heartwood panels. Although the finish appeared unharmed, there were a few dull areas which, under 100X magnification, proved to be minute "crow feet" checking in the film This, again, is a reflection of the severe embrittlement that occurs within the polyurethane finish as it is exposed to ultraviolet light. The film is unable to sustain microscopic strains. Some experiments in which 1 percent of an ultraviolet absorber was incorporated within the film were not encouraging.

A description of boards finished with Rhoplex 34/73 is given in table 10.

The parlele, after 8 weeks in the weatherometer, are shown in figure 9. None of the panels show checking in the wood or finish. The unstabilized panels (N0. 4, column No. 1) show considerable end and edge grain bleaching. Much of the finish here remains glossy; however, numerous fine, bleached streaks are seen at the wood-finish interface. Bleached streaks axe generally absent

Table 9.--Description of representative stabilized sapwood panels with polyurethane finish

No.	Front		Back	
	Stabilization	Finish	Stabilization	Finish
2	None	Polyurethane	None	None
8	1/2-hour diffusion	Polyurethane	1/2-hour diffusion	None
12	5 minutes, 75 pounds per square inch	Polyurethane	None	None



M 126 843

Figure 8.--Ponderosa pine sapwood with two coats of polyurethane finish, after exposure in the weatherometer for 8 weeks. Top row: No surface stabilization; middle row: surface stabilized by pressure; and bottom row: surface stabilized by capillarity.

Table 10.--Description of stabilized sapwood with Rhoplex finish

No.	Front		Back	
	Stabilization	Finish	Stabilization	Finish
4	None	Rhoplex	None	H_2O repellent
9	1/2-hour immersion	Rhoplex	None	None
10	1/2-hour immersion	Rhoplex	None	H_2O repellent
11	1/2-hour immersion	Rhoplex	1/2-hour immersion	None
14	5 minutes, 75 pounds per square inch	Rhoplex	None	None
15	5 minutes, 75 pounds per square inch	Rhoplex	None	H_2O repellent

in the stabilized panels. A closer comparison of the control and diffusion-stabilized panels is shown in figure 10. Still, it is surprising that even in the control, there is considerable area where the wood-finish interface appears unaffected, except for a slight yellowing.

Despite its ultraviolet transparency, the film prevented general severe weathering of the unstabilized wood by excluding liquid water and perhaps, to a degree, oxygen. Stabilization with phenolic resin unmistakably reduces the frequency of occurrence of local fine bleached streaks. In these panels, the finish retained its glossy appearance; there was no checking in the finish or wood. Brush marks are clearly visible in the pressure-stabilized panels (figure 9, Nos. 14 and 15).

Some local brown discoloration is noted in the panels. especially in the pressure-treated ones

Figure 9.--Ponderosa pine sapwood with two coats of Rhoplex finish after 8 weeks in the weatherometer.

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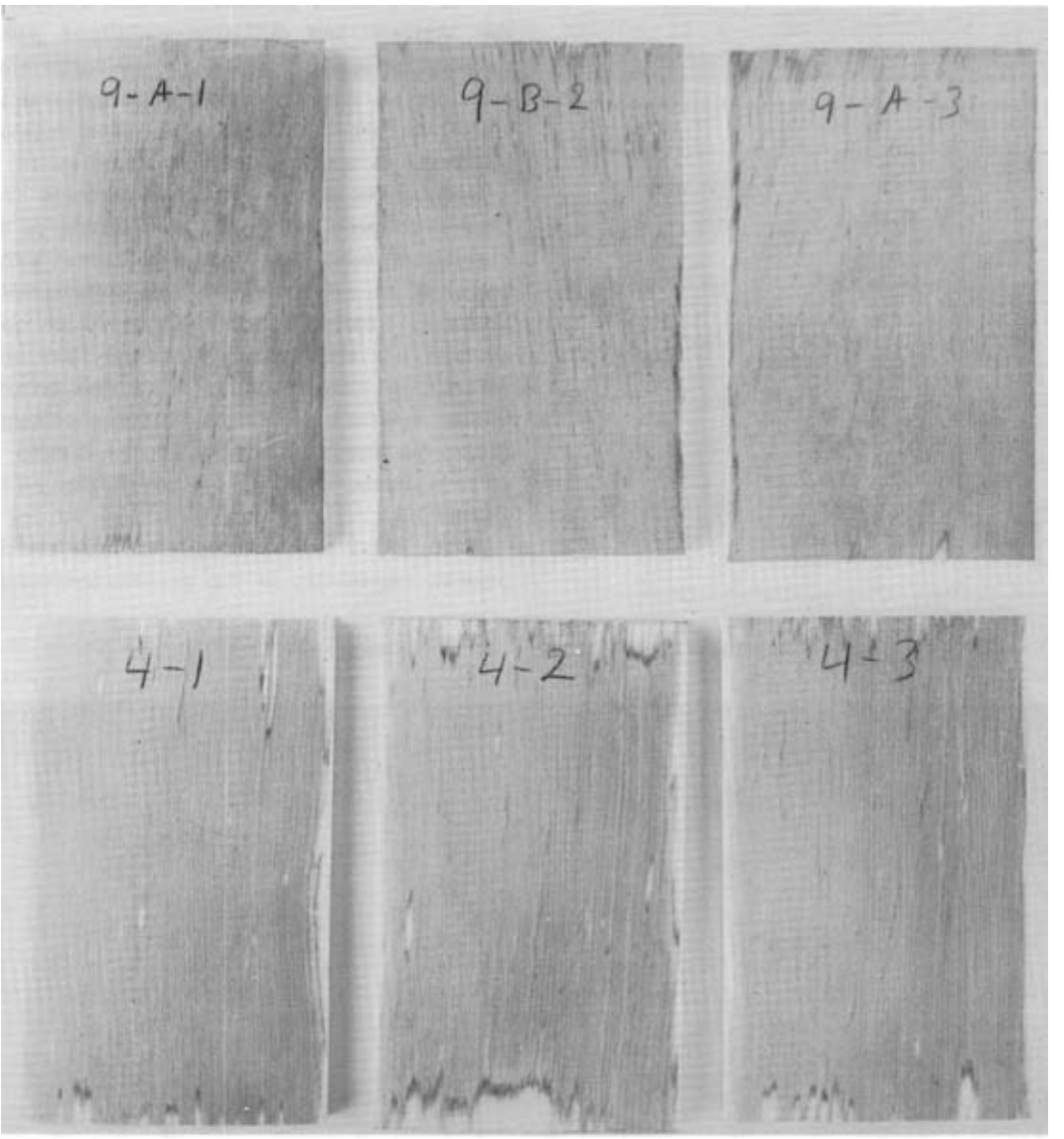

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Figure 10.--Ponderosa pine sapwood with two coats of Rhoplex finish after 8 weeks in the weatherometer.

No. 9--Surface stabilization by diffusion.

No. 4--No surface stabilization,

(Nos. 14 and 15) and needs to be studied further. It is especially interesting that mere immersion in the stabilizing solution (Nos. 9, 10, 11), is sufficient to impart improved weathering characteristics to this particular wood-finish system. Since these Rhoplex films do not become embrittled on weathering, they do not lose their ability to take strains even at relatively high strain rates. Perhaps the function of the phenolic resin at the surface of this system is that of protecting the wood against degradation from ultraviolet light transmitted by the film, instead of that of minimizing surface dimensional movement.

A possible clue to the cause of the occasional fine bleached areas in the nonstabilized panels is obtained on looking at the panels at 100X magnification (figure 11). Tracheids which are clearly seen through the finish seem to be partly filled with finish; that is, in many instances, the

M 128 855

Figure 11.--Photomicrograph (100X) through the clear Rhoplex film an wood. Note that some cell cavities (lumina) are incompletely filled with finish (indicated by arrows). The finish, here, merely bridges over the surface-exposed lumen.

finish merely bridges across a cut-open tracheid and does not fill the lumen. This means that a layer of air is sandwiched between the wood surface (stabilized or not) and the finish. The oxygen here may take part in photo-oxidation when transmitted ultraviolet light strikes the wood. The mass of trapped oxygen is admittedly very small, but the depth of oxidation at the surface need be very small, perhaps less than a micron. Continued replenishment of consumed oxygen could occur by diffusion into the "pockets."

Southern Pine

Southern pine is a fairly dense softwood and was chosen because it weathers badly. Three lots, designated A, B, and C, of commercial flat-sawn sapwood were obtained. The boards were dressed to 3/4-inch thickness. The surface of the A and B boards looked good. The C boards bad a few fine surface checks. The boards were weighed, surface stabilized by either pressure or diffusion treatments, and weighed again before curing. By diffusion, the boards picked up an average of 5 percent of solution (4.0, 4.7, 5.0, and 5.4 percent). By pressure treatment, they picked up 30 percent of solution (24.1, 29.4, 30.4, and 33.4 percent). The average weight of phenolic resin picked up is therefore about 1 and 6 percent, respectively, Owing to the manner of treatment, the resin is very likely present primarily in the surface regions of both faces. Grain raising was noted in the A and C boards. These were lightly sanded but B was not. It is of course, not known how sanding influenced the resin content in the surface region.

Polyurethane and Rhoplex finishes (2 coats) were applied. In an attempt to completely fill the lumina, the Rhoplex was applied in two ways:

a. As before by simple brushing (one face).

b. The board was immersed in the finish, and one stabilized face was worked with a test tube brush to dislodge air and promote penetration of finish into the surface exposed lumina. Inadvertently, of course, both faces were coated with finish The description of representative panels is given in table 11. The panels shown in figures 12, 13, and 14 had weathered 8 weeks. The upper row was finished with Rhoplex. The lower, with polyurethane.

As with the ponderosa pine. surface stabilization is definitely beneficial to the weathering of the finishes on southern pine, The Rhoplex showed less weathering degradation than did the polyurethane. Generally, the severe embrittlement of the polyurethane over the stabilized panels was evidenced by Visible finish checking or as surface dulling, whereas the Rhoplex retained the glossy appearance. Further revealing information is noted in viewing the finish at 65X magnification. Figure 15 shows the polyurethane surface over a seemingly clear, but dull section of panel. Local checking is abundant. Figure 16 shows a Rhoplex surface on a weathered panel. The difference is marked. Examining figure 16 carefully, it will be noted that in spite of the efforts to fill the surface lumina with Rhoplex, there are still unfilled sections. The "white" streaks over the cell walls are actually due to intense reflection of the overhead light.

Table 11.--Description of southern pine sapwood panels

No.	Stabilization	Finish[1]	Result after 8 weeks in weatherometer
A	None	None	
A-4-3	None	Rhoplex, both faces	
A-5-2	1/2-hour diffusion	Rhoplex, both faces	Figure 12, top row
A-6-2	5 minutes, 75 pounds per square inch	Rhoplex, both faces	
A	None	None	
A-4-1	None	Polyurethane	
A-5-1	1/2-hour diffusion	Polyurethane	Figure 12, bottom row
A-6-1	5 minutes, 75 pounds per square inch	Polyurethane	
B	None	None	
B-1-2	None	Rhoplex, both faces	
B-2-1	1/2-hour diffusion	Rhoplex, both faces	Figure 13, top row
B-3-1	5 minutes, 75 pounds per square inch	Rhoplex, both faces	
B	None	None	
B-1-4	None	Polyurethane	
B-2-2	1/2-hour diffusion	Polyurethane	Figure 13, bottom row
B-3-2	5 minutes, 75 pounds per square inch	Polyurethane	
[2]C	None	None	
C-1-3	None	Rhoplex, one face	
C-3-1	1/2-hour diffusion	Rhoplex, one face	Figure 14, top row
C-2-1	1/2-hour diffusion	Rhoplex, one face	
C	None	None	
C-1-1	None	Polyurethane	Figure 14, bottom row
C-3-2	1/2-hour diffusion	Polyurethane	
C-2-2	5 minutes, 75 pounds per square inch	Polyurethane	

[1]"Rhoplex, both faces" means the board was dipped in finish and one face worked with stiff brush to displace air; "Rhoplex, one face" means one face, only, brushed with ordinary brush.

[2]"C" panels were surface checked before treatment.

The Rhoplex finish in the C panels, figure: 14, was applied only to one face by simple brushing. Although there are some checks in the wood, it should be recalled that these boards had some checks in them at the start. From the picturcs, it is not clear whether brushing on the Rhoplex is any better than working it into the surface.

Some of the panels were replaced in the weatherometer for an additional 3 weeks (11 weeks, total). The polyurethane finish continued to deteriorate. The Rhoplex finish that had keen applied by simple brushing continued to deteriorate at the interface only. Although this would seem to indicate an advantage of applying the latex by working it into the surface and filling the lumina, the very good performance of the finish applied in this manner may be due to the finish being present inadvertently also on the back. However, this was shown not to be a factor with the ponderosa pine. Still in the extension of this work, this aspect will be studied in detail.

M 129 835

Figure 12.--Southern pine (board A) after 8 weeks in the weatherometer.

Column 1--No stabilization, no finish.
Column 2--No stabilization, finish only.
Column 3--Stabilization by diffusion, finish applied.
Column 4--Stabilization by pressure, finish applied.

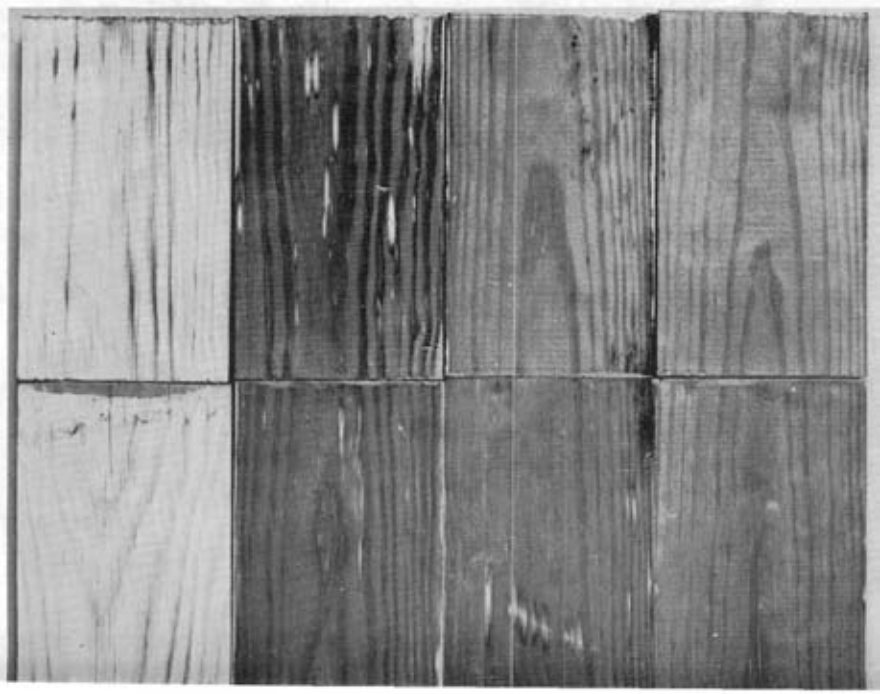
Top row: Finish is Rhoplex, both faces.
Bottom row: Finish is polyurethane, exposed face.

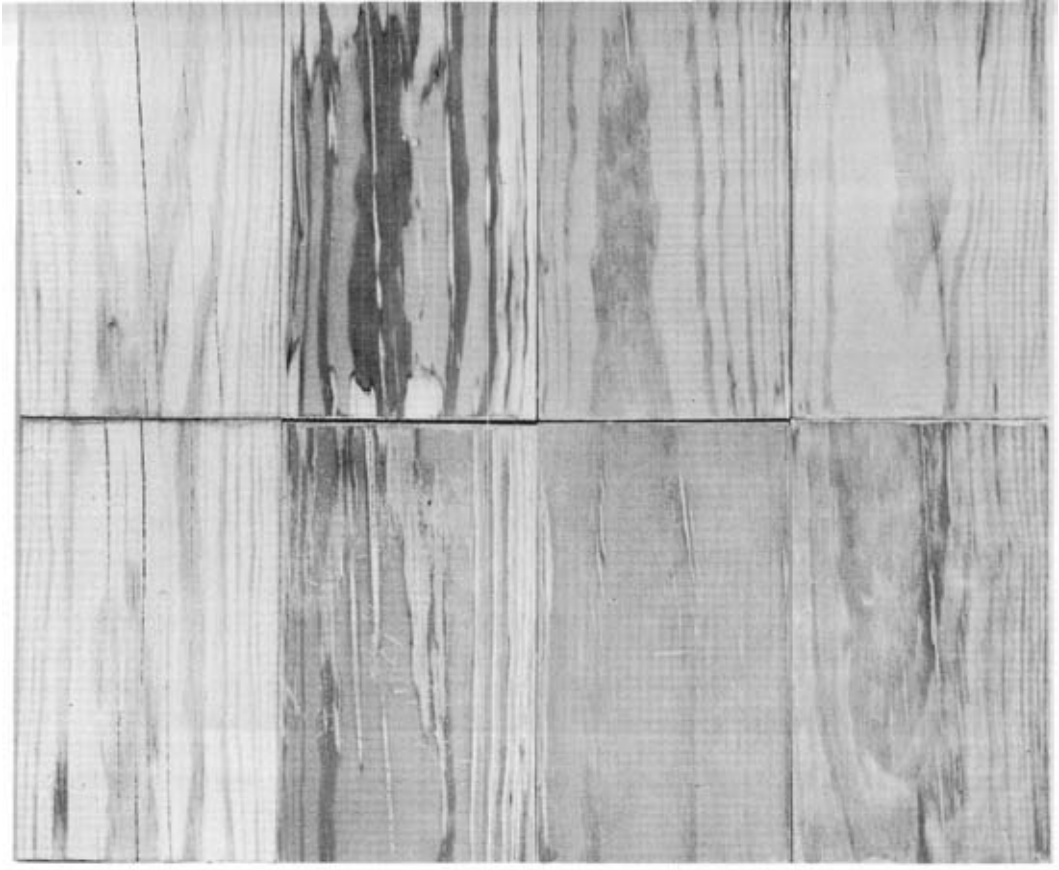
Figure 13.--Southern pine (board B) after 8 weeks in the weatherometer.

Column I--No stabilization, no finish.
Column 2--No stabilization, finish only.
Column 3--Stabilization by diffusion, finish applied.
Column 4--Stabilization by pressure, finish applied.

Top row: Finish is Rhoplex, both faces.
Bottom row: Finish is polyurethane, exposed face.

M 129 838





M 129 840

Figure 14.––Southern pine (board C) after 8 weeks in the weatherometer.

Column 1––No stabilization, no finish.
Column 2––No stabilization, finish only.
Column 3--Stabilization by diffusion, finish applied.
Column 4--Stabilization by pressure, finish applied.

Top row: Finish is Rhoplex, brushed on only one face.
Bottom row: Finish is polyurethane, exposed face.

Figure 15.––Photomicrograph (65X) of weathered polyurethane surface over stabilized wood, showing abundant microchecking.

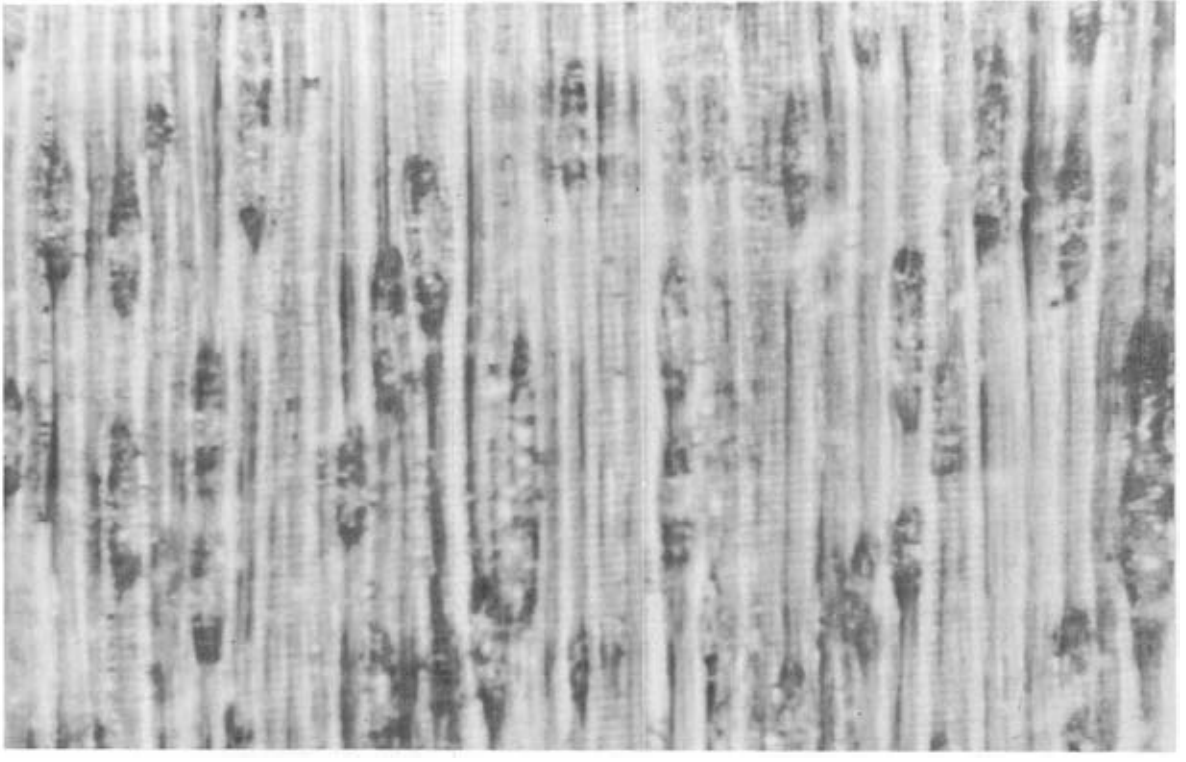


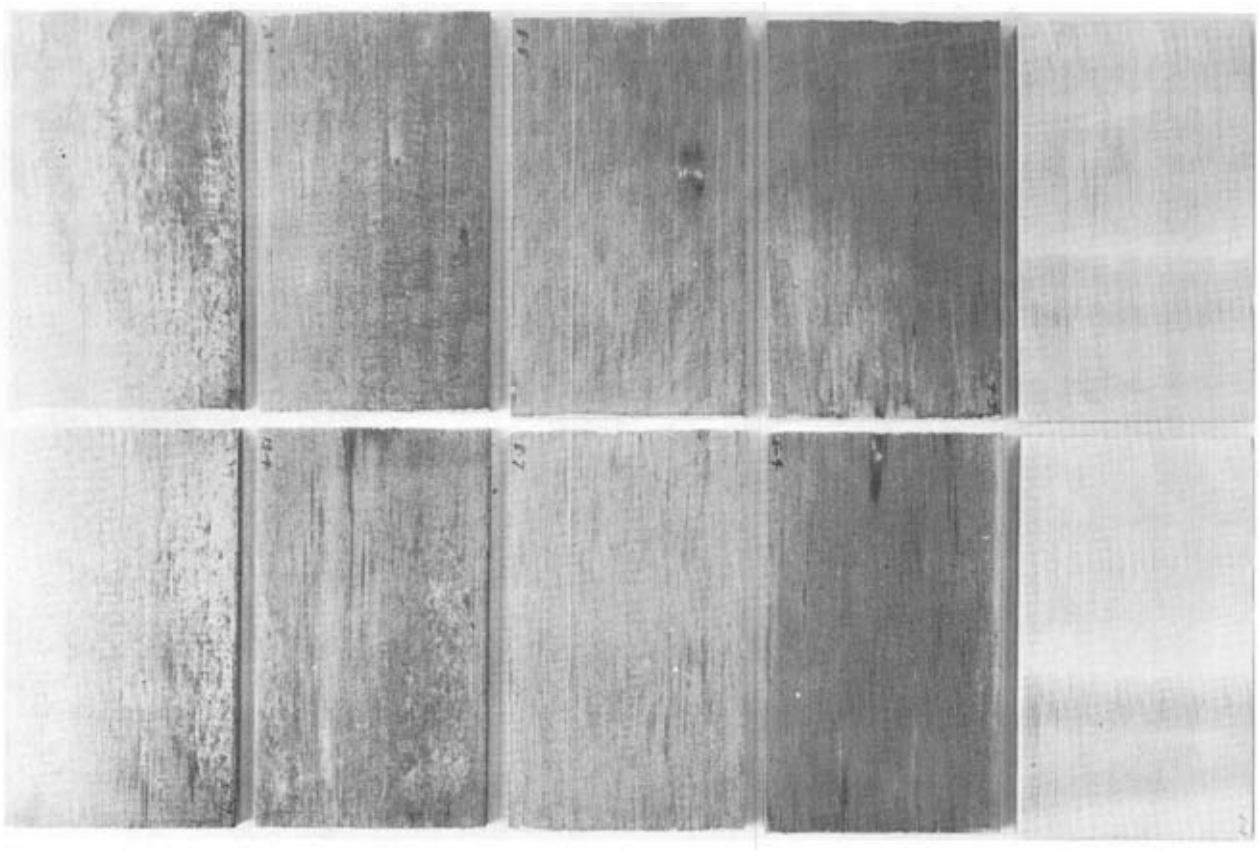
Figure 16.--Photomicrograph (65X) of weathered Rhoplex surface over stabilized wood; note absence of checks.

Redwood

Table 12 gives a description of representative weathered panels made with vertical grain, siding grade redwood. Only the polyurethane finish was used in this series of observations. Figure 17 shows the panels after 6 weeks in the weatherometer. The improvement of the finish with surface Stabilization is obvious. This is especially interesting, since treatment times were only 5 minutes. The absorption of phenolic resin was expected to be as low as that by ponderosa pine heartwood (table 3). Little would be gained by using treating times longer than 5 minutes. Owing to the very small penetration of resin solution into heartwood, it is not likely that the improved weathering performance was due to a true dimensional stabilization. The usual deterioration of the polyurethane over the control (first column) must be due to its interaction with extractives. Somehow, prior treatment with phenolic resin prevents this deterioration, perhaps by laying down an impermeable film. These results maybe related to those found for ponderosa pine heartwood (figure 7). Surface-stabilized redwood, finished with polyurethane and Rhoplex, is now weathering outdoors.

Table 12.--Description of redwood panels

Column No.	Method of stabilization	Finish
1	None	2 coats polyurethane
2	5-minute diffusion into green wood	2 coats polyurethane
3	5-minute diffusion into wood at 90 percent relative humidity	2 coats polyurethane
4	5-minute diffusion into wood at 65 percent relative humidity	2 coats polyurethane
5	None	None



M 124 753

Figure 17.--Redwood panels (in duplicate) finished with polyurethane, after 6 weeks in the weatherometer.

Column 1--No stabilization, two coats polyurethane.
Column 2--5-Minute diffusion of resin into green wood, two coats polyurethane.
Column 3--5-Minute diffusion into wood at 90 percent relative humidity, two coats polyurethane.
Column 4--5-Minute diffusion into air-dry wood, two coats polyurethane.
Column 5--No stabilization, no finish.

DISCUSSION

The observations with the polyacrylate finish over surface-stabilized wood are the most interesting ones made in this study. Specifically, there was a very slight overall yellowing at the interface, but a complete absence of either film or wood checking. Occasionally, there were highly localized brown discolorations. Occasionally, there were fine, bleached streaks at the interface whose frequency of occurrence was reduced when the finish was applied so as to reduce the volume of air trapped in surface-exposed lumina, This must be studied further in detail, since the explanation (displaced air) is ambiguous.

Recent work of Gutfreund (3) on the mechanical properties of fresh films exposed to ozone is pertinent here. He found that a paint based on an acrylic polymer is superior to that based on a styrene -butadiene polymer. The acrylic polymer is related to the latex used in the work reported here and was selected because of its ultraviolet transparency. The styrene-butadiene polymer should be highly absorptive of ultraviolet, since it contains aromatic nuclei. Perhaps the relative performance of the two emulsions could have been predicted simply from a knowledge of the ultraviolet absorption characteristics of the basic polymers,

Work described in the second phase of this work emphasizes the lowered rate of photodegradation

of wood at 3500 A in the absence of air. Perhaps one of the functions of a finish is that of excluding oxygen from the immediate "daylight" surface of wood. Some degradation, of a different kind, occurs in wood even in the absence of air (6). Perhaps the harm from such action is minimized by the presence of the phenolic resin which may preferentially absorb the transmitted energy as suggested by the appearance of the panels in figure 2.

A number of questions remain to be answered:

(1) How do surface-stabilized panels finished with polyacrylate and polyurethane weather outdoors? Panels are now being exposed for such observations.

(2) Do air-filled lumina at the immediate surface promote photo-oxidation? The latexes have appreciable viscosity and surface tension, probably higher than that of the mineral spirits used with the polyurethane. These two factors increase the tendency to trap air in the surface-exposed cell cavities. It is emphasized that the answers to this question is not clear since, inadvertently, both faces received the finish.

(3) Can the curing schedule for the phenolic resin be shortened?

(4) If the function of the phenolic resin, when using ultraviolet transparent finishes, is that of a massive ultraviolet absorber, is it necessary to use a water-soluble resin? Can one use an alcohol- or acetone-soluble resin? Organic solvents should reduce the grain-raising tendency. Grain raising was noted in southern pine and was removed by sanding.

(5) Grain raising is due to improper "dressing" procedures. Can this be minimized by light sanding before treatment?

(6) Instead of phenolic resins, can conventional ultraviolet absorbers be brushed onto the surface of the wood? Recent work by Black of the Forest Products Laboratory, suggests the use of certain inorganic chromium compounds for this purpose.

(7) Are other materials more effective for surface stabilization? Stamm (8) has reported recently on the weathering performance of various finishes over wood stabilized with polyethylene glycol. At the time of reporting, however, too little weathering exposure had occurred to draw conclusions.

(8) If the findings are confirmed, what place do polyacrylate finishes have in southern pine plywood faced with stabilized veneers?

CONCLUSIONS

With the reminder that most of the exposures were made in an Atlas weatherometer, (6 to 12 weeks) two broad conclusions come from this work:

(1) With a clear finish which is sensitive to ultraviolet light and becomes embrittled on weathering, improved durability of the finish, over wood, is achieved if the surface region of the wood has improved dimensional stability. In this way, harmful swelling stresses are not imposed on the embrittled film. With sapwood, such improvement in dimensional stability was obtained by short-time pressure treatment with aqueous 17 percent phenolic resin (5 minutes at 75 pounds per square inch). Simple short-time immersion (1/2 hour) is generally not adequate. With heartwood, a less drastic treatment appears adequate; for example, short-time immersion. Very likely, this is because the intrinsically slow swelling characteristics of the heartwood are further reduced by a resin film at the wood-finish interface. However, even with such treatments, a fine network of checks develops in the finish (seen only at high magnification after about 8 weeks of weathering). One should be concerned about the very long-time performance of such finishes.

(2) With a clear finish such as that based on a "polyacrylate" emulsion or latex, which is not ultraviolet sensitive and which retains its toughness aid extensibility on weathering, good durability is found over phenolic resin-stabilized wood (ponderosa pine and southern pine). Although a slight but uniform color change occurs at the interface, film checking is absent. The wood looks undamaged if the latex is properly applied. Perhaps one of the functions of the phenolic resin, if not the most important one, is to act as a massive ultraviolet absorber fox the light transmitted through the overlying film

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SURFACE CHARACTERISTICS OF WOOD
AS THEY AFFECT DURABILITY OF FINISHES

PART II. PHOTOCHEMICAL DEGRADATION OF WOOD

BY

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SUMMARY

The literature on the photochemical degradation of wood and related materials was reviewed. In the current study it was discovered that volatile degradation products were formed when wood was irradiated, and that visible destruction of the wood substance had occurred on the surface. Quantitative determination of the degradation products was developed into a method for studying the variables in the breakdown precess. Photo-oxidation proved to be an important part of the degradation process in the presence of oxygen, although dissociation of wood a 1 so occurred in an inert atmosphere and in vacuum. Evidence of a post-irradiation effect was observed, and some indications of the effect of wavelength of light were obtained. It was shown that the quantitative measurement of degradation products provided a method for estimating degradation and may be used for a rapid evaluation of means for protecting wood from the effects of light.

INTRODUCTION

It is generally assumed that photochemical degradation of wood is involved in the rapid deterioration of exterior clear finishes on wood as well as in the weathering of unfinished wood. Degradation during exterior exposure is a result of the combined action of all the environmental factors. The effect of light by itself en wood, however, has not been well defined. The object of this work was to explore the photochemical degradation process in wood. It was believed that an understanding of the main principles of the photochemical degradation process in wood could guide future work designed to develop light-stabilized wood and hence lead to materially improved clear finish systems for wood.

A review of the pertinent literature an the degradation of wood and related materials by light is presented, Volatile degradation products were formed from wood during irradiation and a quantitative method of collecting and measuring them was developed. This method was then employed to evaluate the effect of various factors that influence the degradation process. The significance of factors such as wavelength of ultraviolet light, oxygen, humidity, temperature, and wood species was examined. An attempt was made to describe the overall photodegradation process using previously established principles and the results and observations of the work presented here.

[1]The author gratefully acknowledges the contributions of the following members of the Forest Products Laboratory staff who assisted in this work: J. M. Black for his helpful suggestions during this study and on the preparation of this manuscript; R. J. Bayer who performed a number of the experiments; D. B. Johnson who obtained the spectra; M. A. Daugherty for the methoxyl determinations; and C. C. Rankin (Summer Student Trainee from the University of North Carolina) and G. G. King (Summer Student Trainee from Portland State College) for their assistance with other analytical determinations.

LITERATURE REVIEW

Although there are numerous articles in the literature that have a bearing on the photodegradation of wood, relatively few contain significant chemical data. Occasionally information on the degradation of wood by light is included as part of some other study. Sometimes, as in the case of wood weathering, the overall chemical effect is due only in part to sunlight. The greatest volume of published work deals with the degradation of cellulose, usually cotton. To what extent these results are applicable to wood is not known because wood also contains other components, such as lignin, hemicelluloses and extractives, which may interact during irradiation.

Chemical Changes in Wood During Irradiation

Russell effect. --Some indications about the effect of light on wood were found in publications concerning the Russell effect (28).[2] The Russell effect is the action of wood (and other materials) on photographic film in total darkness; it results in an image when the photographic film is developed. After extensive experimentation, Russell concluded that the effect was caused by vapor emitted from wood. Be noted that exposure of wood to sunlight increased the magnitude of the effect on film. For this reason the Russell effect can be looked upon as evidence of light-induced formation of volatile products from wood at ambient temperatures. Russell attributed the effect to hydrogen peroxide, but did not report proof of its presence.

Recently Nambiyar (22) proved the absence of hydrogen peroxide in air that had been passed through sawdust, although this air produced fogging of film. Examination of volatile material condensed from the air stream in a cold trap indicated the presence of acetone and formaldehyde. Previous experiments had shown that formaldehyde could produce fogging of the film This suggests that the Russell effect may be explained by photodegradation and possibly photooxidation of wood, whereby volatile substances are produced that can affect photographic film.

Ground wood irradiation.--A study of the effect of ultraviolet light on wood and lignin was made by Forman (12) and this appears to be the most significant related work to date. Extracted sprucewood meal in sheet form was irradiated in a weatherometer for 85 hours on each side. It was found that the lignin content decreased from 27.5 to 21.1 percent. The methoxyl content in the sample decreased from 4.97 to 3.04 percent and from 15.6 to 10.45 percent in lignin isolated from the sheet. Irradiation (principally at 2537 A) of sprucewood meal with a low pressure mercury arc lamp for 710 hours reduced the lignin content from 27.01 to 22.46 percent, and reduced the methoxyl content in lignin from 16.16 to 14.88 percent. The methoxyl content of wood dropped from 5.03 to 4.52 percent. Irradiation of Braun's native lignin for 216 hours reduced the methoxyl content from 14.81 to 14.20 percent. Willstätter lignin proved to be somewhat more susceptible to irradiation.

Alcohol extraction of irradiated wood meal reduced the lignin content, but increased the methoxyl content of the wood meal slightly. Forman suggested that irradiation either altered the methoxyl groups or decomposed them to volatile products, and that extraction removed material of low methoxyl content, including some that appeared as lignin in the lignin determination. The sample of wood meal that was irradiated for 710 hours had an alcohol-soluble fraction of 4.5 percent and showed a 4.55 percent reduction in the lignin content. A portion of this material was insoluble in dioxane but soluble in water, and capable of reducing Fehling's solution. This portion was believed to be of carbohydrate origin.

The dioxane-soluble portion was separated in ether-soluble and insoluble fractions. The latter had a methoxyl content of 10.6 percent, was similar to native lignin in appearance, and gave a phloroglucinol color reaction similar to those of vanillin and protocatechuic aldehyde. The ultraviolet absorption spectrum of this fraction was similar to that of the total extract (but different from that of lignin) indicating that the ether-insoluble fraction was the major component of the total extract. Extraction of the ether-soluble fraction with a sodium bisulfite solution yielded vanillin, which was identified by its melting point,

[2] Underlined numbers in parentheses refer to Literature Cited on page 59.

color reactions, and ultraviolet absorption spectrum. The presence of vanillin was attributed to photochemical oxidation of lignin. An acidic fraction was also obtained. It included a crystalline material similar in appearance to vanillic acid, as well as resinous material typical of vanilla resins that are found in vanilla extracts. Forman also noted that the ratio of methoxyl content in wood and in lignin to the lignin content of wood remained constant before and after irradiation. Therefore, he concluded that the loss of methoxyl groups was associated with the loss of lignin (as determined. by insolubility in acid). The detection of vanillin and acidic materials indicated that oxidation occurred.

A few years ago Browne of the Forest Products Laboratory also investigated chemical changes during irradiation of ground wood. He exposed finely ground ponderosa pine wood (80 mesh) in a rotating pyrex cylinder to the light of a carbon arc weatherometer. After 11 days of exposure the lignin content was reduced to 77 percent of the original. Additional heating at 110° C. for 11 more days, without irradiation, did not reduce the lignin content significantly. In cellulose, however, a post-irradiation effect has been reported (34) indicating that cellulose behaves differently than wood in this respect. Because of static electricity problems, Browne used slightly larger particles in subsequent experiments. No significant losses in lignin content were noted, however. This was the case in both air and nitrogen atmospheres, as well as in air and nitrogen atmospheres of high humidity. Methoxyl content (an indication of the lignin content) was not significantly altered in either air or nitrogen atmospheres. A slight decrease in the carbon percentage was observed, indicating some oxidation. By infrared spectroscopy an increase in the absorption by the exposed samples at 5.83 microns was detected. This was attributed to an increased carbonyl or carboxyl content. This was reported to be the case when wood was irradiated in either air or nitrogen atmospheres.

Sandermann and Schlumbom (29) irradiated ground wood with light from a high pressure mercury lamp and noted that colored lignin degradation products were formed. Paper chromatography of the alcohol extracts indicated the presence of syringaldehyde and vanillin in ten species of wood. Yellowing of extracted wood was observed and the maximum effect occurred between 305 and 335 millimicrons. Monomeric sugars were not detected.

Chemical Changes in Weathered Wood

Studies of weathered wood contain some information about the chemical changes that have taken place. There is no way, however, of separating the effect of light from the effects of other weathering factors that have acted on wood.

A century ago Wiesner (37) examined weathered wood and reported that the intercellular substance had been lost mechanically (by repeated volume changes because of wetting and drying) and that the chemical behavior had been altered. He concluded that the grayed part consisted of pure or nearly pure cellulose. From microscopic examination of weathered wood he learned that intercellular material was lost in ray cells and vessels first, and only later in the other wood cells. Structural changes included spirally-oriented cracks in cell walls and in pits. It was found that springwood degraded faster, that the hygroscopicity of weathered wood increased as did the ash content, while the density decreased.

In addition to his ground wood investigations described earlier Browne compiled some analytical data on white pine wood that had weathered outdoors for at least 20 years (table 1). These results show that weathering decomposed the lignin and made it soluble. Cellulose appears to have been affected considerably less except perhaps for the topmost layer. Similar results were obtained with various kinds of wood that were exposed on a test fence for 30 years (table 2). In general the water-soluble fraction was greatest in the gray layer and least in the interior. This fraction appeared to consist of partly decomposed lignin and cellulose.

Wood from the various layers was hydrolyzed and the resulting sugars were identified by paper chromatography. From the relative quantities of these sugars it could be concluded that weathesing made xylan and araban soluble more rapidly than glucosan. This was further indicated by the observation that glucose did not predominate in the hydrolyzed water extract, although glucose units do predominate in unaltered wood polysaccharides.

Exposure of thin veneers (0.01 inch) for 14

Table 1.--Analysis of weathered white pine

Material	Extracted by		Lignin	Holo-cellulose	Cross and Bevan cellulose	Ash
	Alcohol benzene	Hot water				
	Pct.	Pct.	Pct.	Pct.	Pct.	Pct.
Gray surface scrapings	3.6	15.9	14.6	58.4	55.5	6.1
Gray and brown surface shavings	5.9	6.2	18.9	62.2	59.5	--
Brown underlayer	5.1	--	24.7	63.0	58.5	.2
Unchanged central portion	5.4	4.9	27.8	62.7	55.0	.2

Table 2.--Analysis of nine weathered woods

Type of wood and component		Extracted samples			Unextracted samples		
Species	Component	Interior	Brown layer	Gray layer	Interior	Brown layer	Gray layer
		Pct.	Pct.	Pct.	Pct.	Pct.	Pct.
Western redcedar	Cellulose	48.0	47.6	44.0	54.4	47.3	43.8
	Lignin	41.9	28.0	7.0	33.0	26.8	9.5
Redwood	Cellulose	48.4	42.5	30.6	45.3	36.6	28.3
	Lignin	53.2	35.4	10.9	41.0	32.6	16.4
Cypress	Cellulose	50.5	53.8	53.4	51.8	50.0	50.5
	Lignin	41.8	31.1	2.9	35.1	26.1	4.6
Douglas-fir	Cellulose	50.1	45.6	47.1	49.3	49.8	52.7
	Lignin	36.1	30.4	6.9	33.7	28.7	5.6
Ponderosa pine	Cellulose	50.7	51.6	48.7	53.8	58.4	44.2
	Lignin	50.0	21.1	3.7	27.7	21.4	6.0
Southern pine	Cellulose	50.5	52.2	51.0	52.2	51.1	49.1
	Lignin	50.0	21.1	3.7	30.5	20.0	7.4
White pine	Cellulose	57.6	57.0	44.4	40.4	58.1	43.6
	Lignin	33.3	24.7	12.9	29.1	24.0	10.9
Yellow-poplar	Cellulose	50.6	59.0	61.7	49.5	63.7	64.2
	Lignin	27.4	14.6	1.5	22.3	16.2	1.5
Birch	Cellulose	54.5	57.2	60.0	46.9	56.4	70.3
	Lignin	27.8	21.0	6.4	20.5	16.8	3.7

Table 3.--Chemical changes in wood exposed to sunlight (27)

Item	Spruce		White birch		Poplar	
	Original	Exposed	Original	Exposed	Original	Exposed
Copper number	6.2	25.2	5.2	15.7	3.8	19.5
Lignin (Pct.)	28.14	28.2	22.80	20.20	24.56	15.85

days in the weatherometer produced detectable chemical changes in wood. Although the veneers were exposed on one side only, the solubility in water increased by 1.46 percent and the lignin content decreased by 0.72 percent.

Richter (27) exposed thin (1/16 inch) wood samples to sunlight for 100 hours on each side and found certain chemical changes (table 3) in the scrapings from the surface. When placed in water, the exposed wood scrapings turned the solution deep yellow, indicating that some of the reaction products were water soluble.

The penetration of light into wood was studied by Browne and Simonson (3). They found that infrared light penetrated deeper than visible light, while the penetration of ultraviolet light was negligible. For instance, 17.4 percent of visible light (400 to 750 millimicrons) penetrated Western larch to a depth of 0.02 inch, while only 0.016 percent of the light penetrated as far as 0.1 inch.

Color Changes in Wood and Fiber

Schramm (33) reported color changes (yellowing) in several species of wood resulting from sunlight exposure, and recognized that it was a photochemical process, possibly dependent on the presence of oxygen. He concluded that the cellulose portion of wood and the substances colored by iron or browned by ammonia were not responsible for yellowing.

Schramm also studied graying of wood in outdoor exposure (32). He attributed the gray color in part to iron salts. Analyses showed the presence of iron in gray but not in browned or yellowed woods. Iron salts such as sulfate produced color artificially.

In most of the previously mentioned studies color changes of wood resulting from irradiation have been described. It is, however, difficult to estimate to what extent the color changes are an indication of the degradation process. A comprehensive study of the color changes of numerous wood species, especially furniture woods, was reported recently by Sandermann and Schlumbom (30).

The problem of light damage to wood surfaces and means of protection has also been discussed by Schlumbom (31). In addition to a review (55 references) some data were given on the wavelength dependence of maple discoloration. Maximum effect was noted at 330 millimicrons and a minimum at 310 millimicrons. Degradation characteristics of various coating materials were also listed along with effective ultraviolet light absorbers for them.

Jute fiber contains some lignin, and its discoloration upon exposure has been attributed to the lignin portion (5). Demethoxylation was thought to yield polyhydroxy phenolic materials, that were converted to quinones, providing the color. Acetylation prevented this discoloration, and it was suggested that the quinoid forms could not be formed after acetylation.

Degradation of Groundwood Paper

Other work relating to the light stability of wood dealt with the discoloration (fading) of groundwood paper (19). It was observed that pH in the range from 3.5 to 4.5 was most effective in preventing degradation of the lignocellulose by light from a weatherometer. Other work on the fading of groundwood handsheets by light of a mercury arc indicated that fading was faster in the presence of atmospheric oxygen and much faster when ozone was present (23). Ozone alone, however, caused bleaching. Therefore, it was suggested that either

ozone participated in the photochemical reaction, or that the reaction producing the discoloration actually was a photochemical oxidation reaction. High humidity and temperature appeared to favor the discoloration reactions. The absorption spectra of lignin derivatives were similar to the spectral sensitivity curves of the groundwood handsheets. This was an indication of the participation of lignin in the fading reaction. Several wavelengths of ultraviolet light appeared to be particularly effective: 365, 334.2, 313.2, and 302.2 millimicrons.

More analytical data on the fading of groundwood sheets with a carbon arc fadeometer have been reported (20). The irradiation of groundwood sheets for 10 hours on each side produced marked effects (table 4). Changes occurred in the lignin, as shown by both the decrease of the lignin content and the decrease of the methoxyl group concentration in lignin. Significant changes in the cellulose portion of the sheets were indicated by the increased copper number and decreased cellulose content. Similar exposure of sulfuric acid (Klason) lignin resulted only in a small decrease in its methoxyl content. It was concluded that lignin in the groundwood sheets was much more reactive photochemically than the isolated lignin. Exposure of groundwood sheets to summer sunlight for 73 hours (table 5) produced an effect similar to that of the artificial source.

The large solubility increase in dilute (1 percent) NaOH as a result of irradiation is noteworthy. In the waged sheets 80 percent of the original lignin remained in the sheet after extraction with the base. In the aged sheets only 57 percent of the original lignin was present and after extraction with the dilute base only 7 percent remained. Thus, sunlight altered the lignin so as to make most of it soluble in dilute alkali. The increase in the uronic acid content was interpreted as an indication of carbohydrate oxidation.

Degradation of wood by sunlight has also been mentioned by Richter (27) in a study of the light stability of various papers. Fold retention, copper number, pH, viscosity, solubility, weight loss, and cellulose content determinations were used to measure the degradation of paper. Exposure to sunlight reduced the fold retention, pH, viscosity, cellulose, and lignin content, while solubility in alkali and copper number were increased. Weight losses of 1 to 2 percent also were recorded Several atmospheres were tested and the extent of degradation increased in this order: hydrogen, carbon dioxide, air, dry oxygen, moist oxygen. Window glass, a poor transmitter of ultraviolet light, offered some protection. Several chemicals were examined for their effect on the degradation process. Sodium stannate and magnesium hydroxide had a protective effect, while ferrous and ferric oxalates appeared to catalyze degradation.

Table 4. --The effect of Fade-Ometer exposure of groundwood sheets (20)

Item	Unexposed	Exposed	Difference
Copper number	2.55	14.14	+11.59
Cross and Bevan cellulose (Pct.)	59.7	52.7	- 7.0
Pentosans (Pct.)	12.4	10.7	- 1.7
Lignin (Pct.)	27.3	23.8	- 3.5
Methoxyl in lignin (Pct.)	15.67	13.10	- 2.57
Solubility in ethanol-benzene (Pct.)	0.6	4.1	+ 3.5
Solubility in 1 percent NaOH (Pct.)	12.4	38.4	+26
Solubility in petroleum ether (Pct.)	0.32	0.12	- 0.2

Degradation of Cellulose

The degradation of cellulose by light has been studied extensively, and considerable information is available. This is of interest when wood is studied because cellulose is its major component., However, there are some indications that the degradation of the cellulose component during wood irradiation differs from the degradation of pure cellulose. Therefore, an assumption that both processes are identical is unwarranted.

Pure cellulose is not a good absorber of ultraviolet light and some question exists about the nature of the absorbing functional groups. That some ultraviolet light is absorbed by cellulose, however, is shown by the existence of cellulose fluorescence. Toner and Plitt (36) reported the fluorescence of purified cotton cellulose in the near ultraviolet at 365 millimicrons when excited by radiation of 270 millimicron wavelength. The introduction of carboxyl and reducing groups in the cellulose resulted in fluorescence quenching, whereas reduction of the cellulose with borohydride caused a twofold increase in the intensity of fluorescence.

Sugars.--It has been suggested that the acetal chromophore in cellulose absorbs ultraviolet light. The kinds of sugars isolated by Beelik and Hamilton (1) from purified wood cellulose that was irradiated appear to support that suggestion. The products obtained included volatile and nonvolatile acids, and the following sugars were identified by paper chromatography: xylose, xylobiose, -triose, -tetraose, and -pentose: D-glucose, cellobiose and -triose; D-arabinose, 3-ß-D-glucosido-D-arabinose, 3-ß-cellobiosido-D-arabinose, and mannose. The presence of D-arabinose (a pentose) was interpreted as evidence of photolysis of the bond between C_1 and C_2 of the D-glucose units in cellulose:

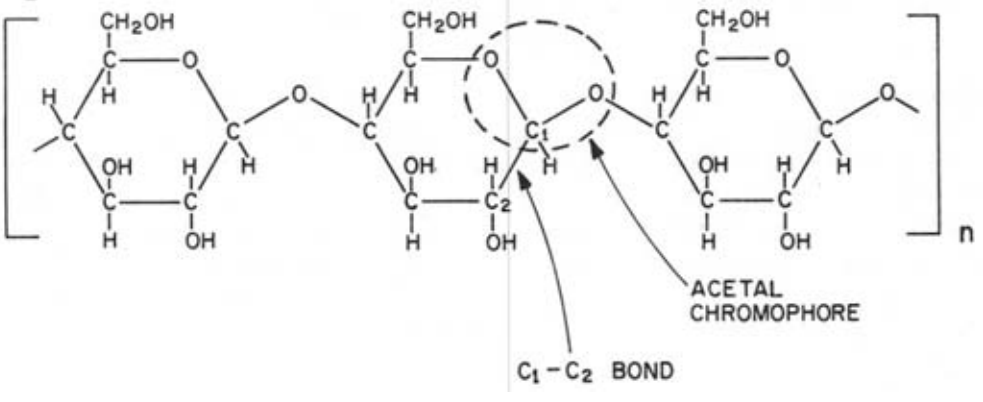
Table 5.--Effect of exposure of groundwood sheets to summer sunlight (20)

Item	Unexposed	Exposed
Copper number	5.4	19.3
Cross and Bevan cellulose (Pct.)	80.9	81.7
Pentosans (Pct.)	0.5	1.0
Lignin (Pct.)	9.9	5.6
Methoxyl in lignin (Pct.)	14.1	8.6
Solubility in ethanol-benzene (Pct.)	1.9	4.7
Solubility in 1 percent NaOH (Pct.)	19.5	39.3
Uronic acid (Pct.)	0.5	1.0

Additional work that supports this mechanism of degradation bas recently been reported by Gingras and coworkers (14).

It is interesting to note that in the previously mentioned work by Sandermann and Schlumbom (29) it was stated that no simple sugars were obtained by wood irradiation. This suggests a possibility of lignin-cellulose interaction during photodegradation, resulting in the formation of different end products from wood cellulose,

Free radicals and post-irradiation reactions.--The formation of free radicals during cellulose photodegradation has been suggested. Recently Kleinert (17) demonstrated by electron spin resonance spectroscopy the generation of free radicals in purified wood cellulose with ultraviolet light, and observed their stability. He found that the radical concentration increased with time of irradiation, and was related to the peroxide content and to cellulose chain splitting. It was suggested that the primary reaction during cellulose irradiation was chain splitting which resulted in free radical formation followed by



reaction with oxygen to form peroxidic radicals. Cellulose samples were also irradiated under atmospheres of oxygen, nitrogen, and in vacuum. The largest concentration of radicals was obtained in vacuum, the smallest in oxygen. Storage of irradiated samples for 150 days caused a disappearance of free radicals in samples exposed to oxygen and nitrogen, while the concentration in the sample under vacuum was reduced to about 10 percent. This indicated that reactions took place for some time after the irradiation (post-irradiation effect).

Stillings and Van Nostrand (34) reported that the irradiation of cellulose with ultraviolet light produced an increase of the copper number, a reduction of the α-cellulose content, and degree of polymerization. In addition, volatile products were formed: carbon monoxide, carbon dioxide, and water, In this case, heterogeneous ultraviolet was used, and the presence of oxygen caused more severe degradation. A post-irradiation effect was observed; cellulose that was stored in air after irradiation in a nitrogen atmosphere showed a continuing decrease in the degree of polymerization.

Effect of various atmospheres on degradation.--Launer and Wilson (18) described the effect of water vapor and oxygen on cellulose degradation in near (mostly 388 millimicrons) and middle (254 millimicrons) ultraviolet. In the middle ultraviolet region, water inhibited degradation and oxygen had no effect. In the near ultraviolet, oxygen and water accelerated degradation. In addition, cotton and wood cellulose reacted differently. Thus in the presence of water vapor wood cellulose suffered a greater drop in its α-cellulose content than cotton cellulose,

Flynn and others (11) described the results of cellulose irradiation in vacuum In addition to carbon monoxide and dioxide, hydrogen was detected by mass spectrometry. Quantum yields (the number of molecules produced per quantum of light absorbed) of 10^{-2} for hydrogen formation and 10^{-3} for carbon monoxide plus carbon dioxide were calculated. Flynn and Morrow (10) also found that the quantities of hydrogen formed corresponded closely to the number of aldehyde groups generated, suggesting that hydroxyl group photolysis (in spite of absence of light absorption by hydroxyls at the wavelength used) was the mechanism whereby aldehyde groups and hydrogen were obtained, It was further noted that oxidized cellulose was more susceptible to degradation, unless neutralized with a base. In addition, one and three carbon hydrocarbons were detected among the degradation products.

In further experiments (9) cellulose with deuterated hydroxyl groups was used. Most of the hydrogen formed was HD (very little D_2). This suggested that disproportionation rather than atom abstraction or combination accounted for hydrogen formation. It was observed that hydrogen, carbon monoxide, and carbon dioxide formation increased with temperature: the conclusion was that these substances arose from photolysis of functional groups as well as radical depropagation. Chain scission and carboxyl group formation was attributed to oxidation of long-lived oxygen-containing radicals after irradiation, while aldehyde groups presumably were formed by photolysis or by disproportionation of radicals.

Egerton and others (6) noted increased photodegradation of cellulose at higher temperatures in oxygen, as indicated by increased fluidity. The reverse was true in a nitrogen atmosphere. High humidity was found to reduce the loss of tensile strength; this is in accord with the previously mentioned (18) inhibition of hydrogen evolution by water vapor. Another mechanism study was described by Zapolskii (38), and the formation of an α-diketone group in cellulose as a result of irradiation was suggested. Recently, a review based on theoretical considerations has been published by Phillips and Jett in two parts: I, Primary Processes in Model Systems (24), and II, Photodegradation of Cotton Cellulose (as). This review (139 references) included a discussion of the primary photochemical processes and an examination of existing knowledge of cellulose photodegradation.

Summary of Literature Review

It is seen that despite the considerable volume of related previous work, numerous questions and uncertainties remain about the details of photodegradation processes of complex natural materials such as wood and cellulose. This is especially true for wood, where little prior work has been done on photodegradation and where the chemical structure of the material itself is not

well characterized. From pure cellulose by irradiation with ultraviolet light mono- and oligosaccharides were obtained, as well as acids and gaseous products. An increase of reducing groups was also detected. In wood a decrease in methoxyl content, carbonyl absorption, and the Cormation of lignin fragments (vanillin, syringaldehyde) was observed. On the other hand, no sugars or volatile products were reported among the degradation products of wood. Little is known about the factors influencing wood photodegradation, the nature of the process beyond the indications of lignin oxidation, and the role in the degradation of the various wood components and their interaction, if any,

EXPERIMENTAL PROCEDURES

This section describes in detail the procedure and apparatus used in evaluating the photochemical degradation of wood. In the next section, Results and Discussion, only a brief description of test methods is given to identify the process so that further details could be confined to this section,

Sample Preparation

Ground wood.--Ground wood samples were prepared by grinding kiln-dried lumber in a Wiley mill. The particles were separated according to size with standard sieves. Ground wood in the 40-60 mesh range (250-420 microns) was used; the sample weight, unless otherwise stated, was 40 grams for each determination.

Extracted wood.--Samples of extracted wood were obtained by successive extraction of ground wood in a soxhlet extractor with a 1:2 ethanol-benzene mixture (4 hours), then with 95 percent ethanol (4 hours), followed by digestion with water at 100° C. (3 times), and drying at room temperature.

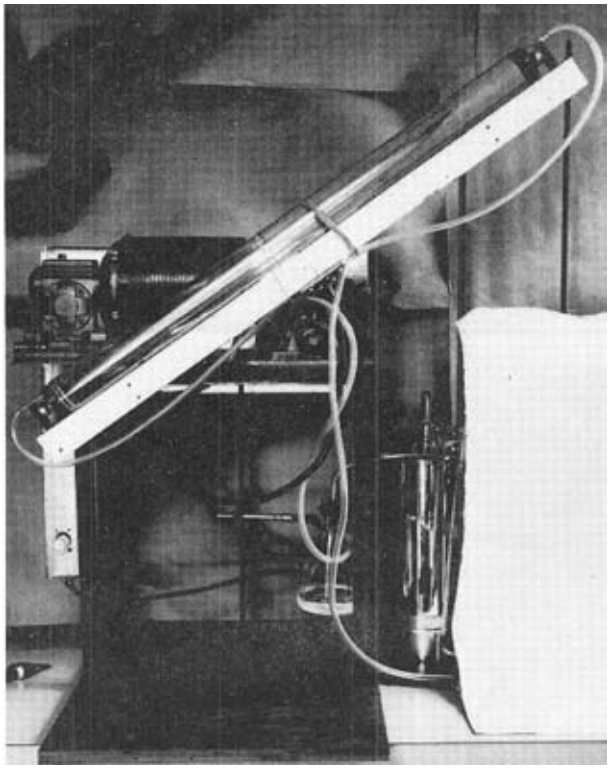
Veneer.--Thin veneer samples (15 by 75 centimeters) were cut from flitches of green wood with a veneer slicer, and then dried in a veneer dryer, The thickness of yellow-poplar veneer was about 0.2 millimeter; other veneers (Douglas-fir and redwood) averaged about 0.25 millimeter in thickness.

Apparatus for Ground Wood Irradiation

Ground wood was irradiated in a reaction chamber that consisted of a tubular light source enclosed by a larger Pyrex tube (figure 1). Ground wood was placed in the tube and was free to move as the apparatus oscillated through 180°. Thus, the ground wood was mixed as it fell from one end of the reaction chamber to the other past the light source. A slow stream of gas was passed through the chamber to provide the desired atmosphere. The emerging gas stream was passed through a dry ice-acetone cooled cold trap and then through gas absorption tubes that are described later.

The light source for ground wood irradiation was a 30-watt General Electric G30T8 germicidal lamp. It provided ultraviolet light primarily at a wavelength of 2537 A {angstroms). This type of light source was also used in other experiments where a 2537 A light source is specified. According to the manufacturer, the spectral energy

Figure I.--Oscillating apparatus for irradiation of ground wood. M 124 442



distribution of this lamp was as shown in the following tabulation:

Wave Length A	Watts
2400 - 2600	8.34
2600 - 2800	0.01
2800 - 2900	0.02
2900 - 3000	0.03
3000 - 3100	0.02
3100 - 3200	0.16
3200 - 3400	0.01
3400 - 3600	0.01
3600 - 3800	0.17
3800 - 4000	0.01
4000 - 5000	0.66
5000 - 6000	0.33

Apparatus for Veneer Irradiation

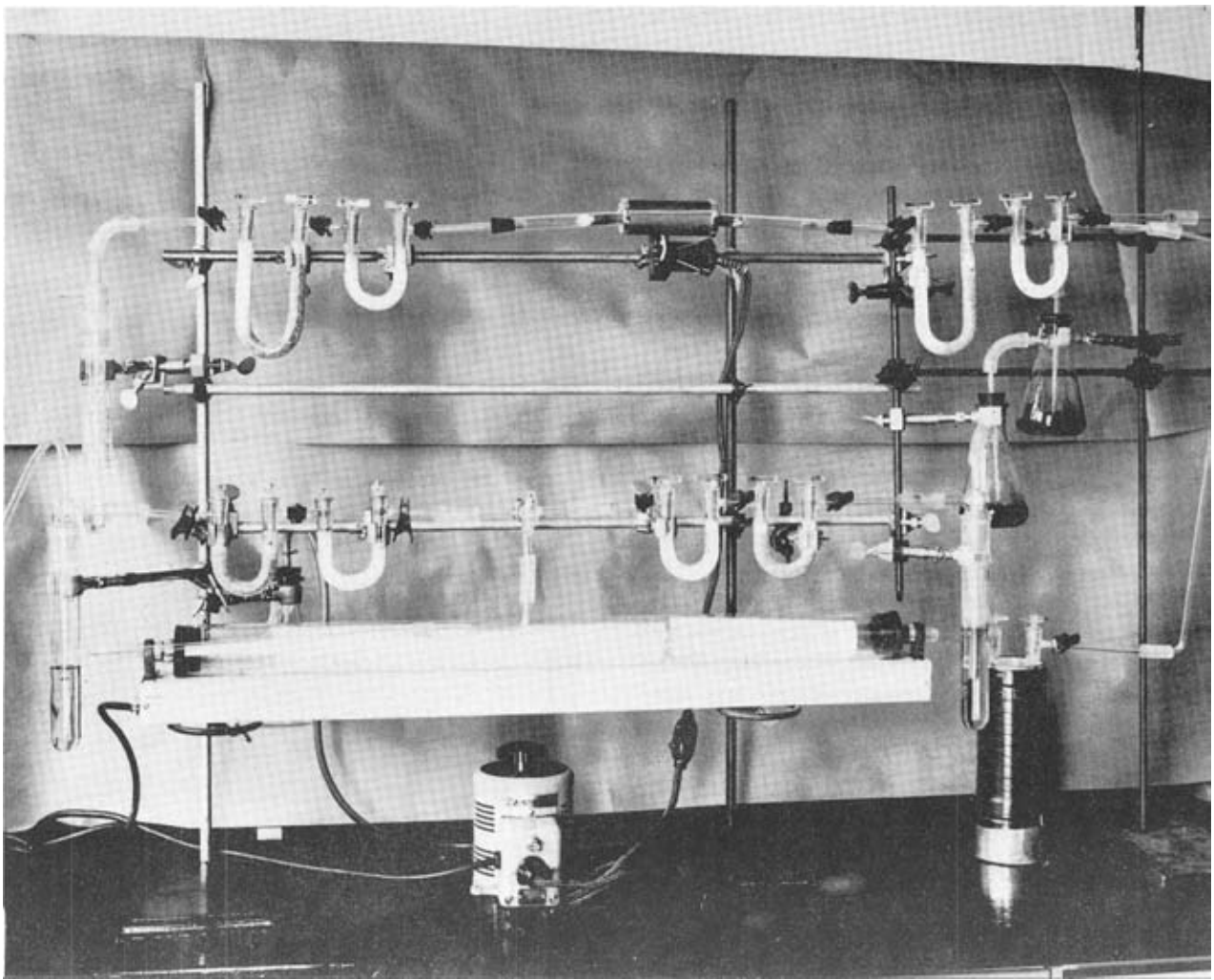
Veneer was irradiated in two types of apparatus each of which could be equipped with two different light sources depending on the determinations to be made. Thus, four arrangements for irradiating veneer were available.

One type of apparatus utilized tubular light sources enclosed by a larger Pyrex tube (figure 2). The veneer was placed between the light sources and the Pyrex tube and a slow stream of gas was passed through the chamber to provide the desired atmosphere. The emerging gas stream was passed through a dry ice-acetone cooled cold trap and then through the gas analysis apparatus that is described later.

The two light sources used in this apparatus were the 2537 A germicidal lamp described earlier fer ground wood irradiation and a near ultraviolet or "blacklight" lamp designated as a 30-watt TF 30 BLB Raymaster lamp (George Gates and Company, Franklin Square, Long Island, N.Y.). According to the manufacturer, the blacklight lamp emits wavelengths from 3000 to 4100 A with a peak output at about 3650 A. It was used in evaluations of the effect of species, ultraviolet

Figure 2.--Apparatus for irradiation of veneer, showing the irradiation tube, the gas purification system above it, and the gas absorption apparatus at the top.

M 127 305



light absorbers, and humidity.

The second type of apparatus for irradiating veneer was the Srinivasan-Griffin Photochemical Reactor (Southern New England Ultraviolet Company, Middletown, Conn.). The irradiation chamber in this apparatus (figure 3) differed from the apparatus described earlier in that the light sources (16 small tubes) were located around the perimeter of the chamber rather than in the center. For optimum transmission of ultraviolet light a quartz tube was used to hold the veneer sample and allow control of the atmosphere.

The reactor was used in evaluating the effect of temperature during irradiation of veneer. It was equipped with a cooling fan which, when turned off, raised the temperature in the irradiation chamber from 55° C. to 90° C. The photochemical reactor was also used to irradiate veneer in a vacuum. The quartz irradiation chamber was connected to a vacuum manifold. Two sample collection tubes, one for gas, and another for condensate at liquid nitrogen temperatures, provided material far analysis. Both samples were examined by gas chromatography.

Two types of interchangeable lamps were used in the photochemical reactor to determine the effect of wavelength on irradiated veneer. The blacklight lamps had an intensity at the center of the reactor of 9,200 microwatts per square centimeter or 1.5 to 5 x 10^6 photons per second per cubic centimeter, according to the manufacturer's data; the spectral energy distribution is shown in figure 4.

Figure 4.--Spectral energy distribution of blacklight lamps used in the photochemical reactor.

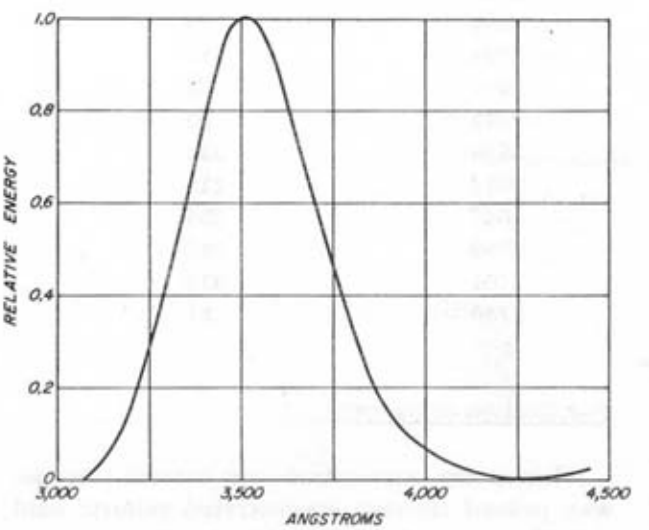
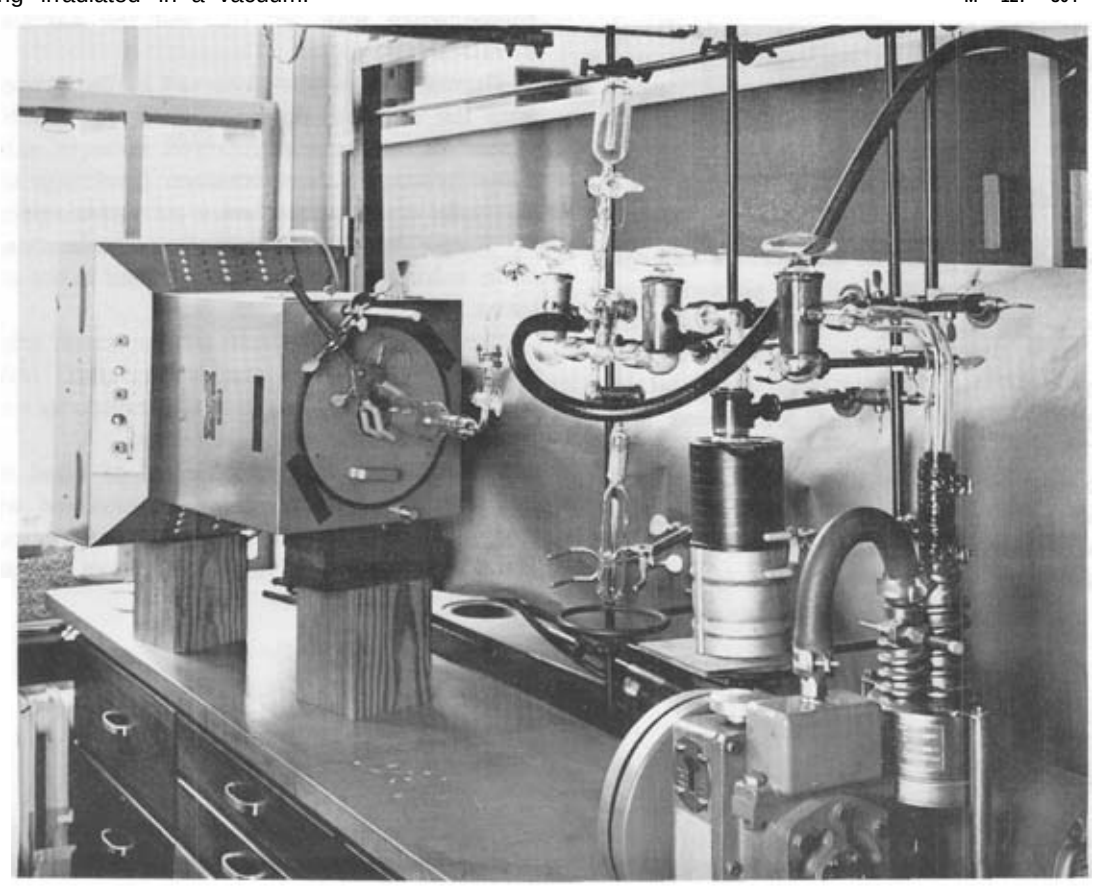


Figure 3.--The photochemical reactor for irradiating veneer is shown at the left. 4 quartz tube in the center of the reactor contains the veneer sample which in this arrangement is being irradiated in a vacuum. M 127 304



The second set of lamps had a peak emission at 2537 A and an intensity of 1.65 x 10^6 photons per second per cubic centimeter; the energy distribution of these lamps is given in the following tabulation:

Wave Length A	Microwatts per square centimeter
2537	12800
2652	388
2804	14
2894	18
2967	66
3022	32
3129	250
3654	213
4047	250
4359	768
5461	418
5780	91

Purification of Gases

When a dry atmosphere was desired, the gas was passed through concentrated sulfuric acid and then through a tube filled with anhydrous magnesium perchlorate. When nitrogen was used, it was bubbled though Fieser's solution (8, p. 299) to remove any oxygen present. To remove carbon dioxide, the oxygen, air, and nitrogen gases were also passed through a tube filled with Ascarite.

Chemical Analysis

Gaseous Products.--The gas stream emerging from the irradiation chamber was passed through an acetone-dry ice cooled condenser, and then through gas absorption tubes. as shown in figure 2.

The gas absorption tubes were equipped with ground-glass ball-and-socket joints and stopcocks. This permitted easy handling and prevented error due to absorption of moisture and carbon dioxide from the air. Carbon dioxide was collected with Ascarite. Hydrogen and carbon monoxide were oxidized to water and carbon dioxide, respectively, by passing the gas stream over copper oxide heated to 300° C. Water vapor was collected with anhydrous magnesium perchlorate.

Condensate.--The material in the dry ice-acetone cooled cold trap was routinely examined by gas chromatography. A glass column (2 meters long, 4 millimeters in diameter) was used for the analysis of methanol. The solid support was Teflon 6 coated with 10 percent Ethofat 60/25 (polyoxyethylene glycol stearate, made by Armour Industrial Chemical Company). The column temperature was 120° C. and the flow rate of helium carrier gas was 35 milliliters per minute. The gas chromatography apparatus was a Perkin Elmer 154-E.

The condensate was largely water. The amount of methanol present was determined from a graph of peak height plotted against concentration that was obtained from chromatograms of known concentrations of methanol in water. In addition to methanal, an unknown compound having a shorter retention time (like that of ether) was noted. A typical chromatogram is shown in figure 5.

The condensate in the cold trap cooled by liquid nitrogen was analyzed in the vapor phase by gas chromatography for the presence of hydrocarbon gases (methane, ethane, ethylene). A Perkin-Elmer column "J" containing silica gel was used. The flow rate of helium carrier gas was 18 milliliters per minute, the column temperature was 50° C., and the sample was 2 milliliters.

Formaldehyde was detected in the condensate with the chromotropic acid test (7), which consisted of adding concentrated sulfuric acid and 4,5-dihydroxy-2,7-naphthalene disulfonic acid to the unknown. A purple color proved the presence of formaldehyde. Quantitative estimation was done colorimetrically as described in the article cited.

The presence of formic and/or acetic acid was indicated by paper chromatography, although further resolution of the acid mixture by various solvent mixtures was not attained.

Measurement of pH.--The pH of wood before and after irradiation was determined with a Beckmam H2 pH meter, using a suspension of 1 gram of ground wood in 10 milliliters of distilled water.

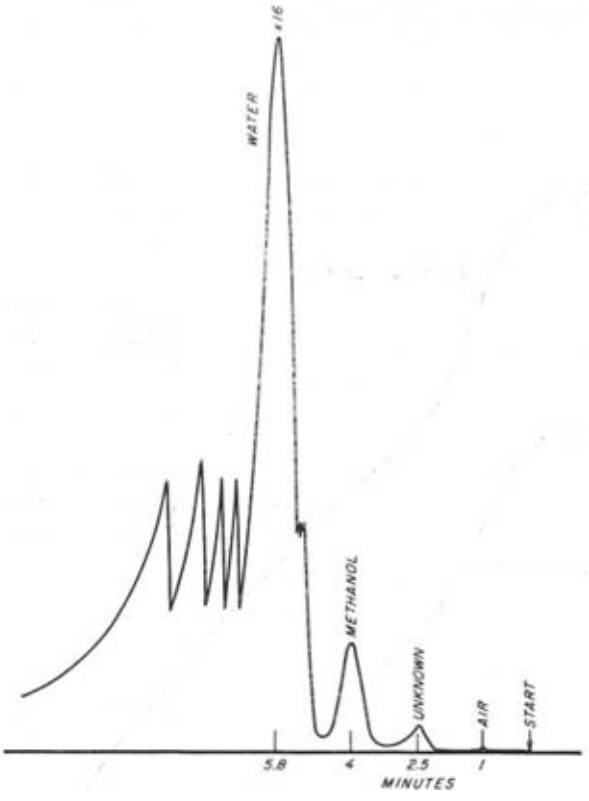


Figure 5.--Chromatogram of condensate from Douglas-fir resulting from irradiation.

Absorption Spectra

Infrared.--Ground wood samples were mixed with potassium bromide and pressed into pellets. The infrared absorption spectra were obtained on a Baird AB-1 spectrophotometer with sodium chloride prism optics.

Ultraviolet.--The ultraviolet absorption spectra were also obtained with the samples in a solid state. Ground wood and lignin samples were mixed with potassium bromide and pressed into pellets. A Beckman DK-2 ultraviolet spectrophotometer was used.

RESULTS AND DISCUSSION

The purpose of this work was to gather information that might contribute to the understanding of the photodegradation process of wood. Some of the results of this work, together with the previously cited information, provide the basis for a sketch of the events that occur when wood is exposed to light. These events will be discussed in their natural sequence, beginning with the interaction of light and wood.

The light that strikes a wood surface may be reflected, scattered, transmitted or absorbed, and chemical changes in the wood may result. Therefore a knowledge of the light absorption characteristics of wood are important for an understanding of its reaction to light. The generation of free radicals in wood by light illustrates the reactive intermediates through which wood is degraded to volatile end products. By quantitative measurement of these products the importance of factors such as temperature, wavelength, oxygen concentration, and types of wood was explored.

Interaction of Light and Wood

When a substance is exposed to light, the light may be reflected, transmitted, or absorbed. If the light is absorbed, the energy of the photon is captured by the absorbing molecule. The level of energy of the photon is dependent upon the wavelength and is expressed by the following equation:

$$E = h\nu = h\frac{c}{\lambda}$$

where, E = energy
h = Planck's constant
v = frequency
λ = wavelength
c = velocity of light

As the wavelength decreases, the amount of energy per photon increases. It is known that wood absorbs certain wavelengths and reflects others in the visible range; this is indicated by the various colors of wood. It has been observed by Wengert of this Laboratory, that in the near ultraviolet range from 4000 to 3500 A, as the wavelength of light decreased, the reflectance of wood decreased.

An ultraviolet absorption spectrum of Douglas-fir wood was obtained and the decreasing reflectance is attributed to increasing absorption of light. Figure 6 shows the relationship between wavelength and light absorption for Douglas-fir; the absorption spectrum for softwood lignin is

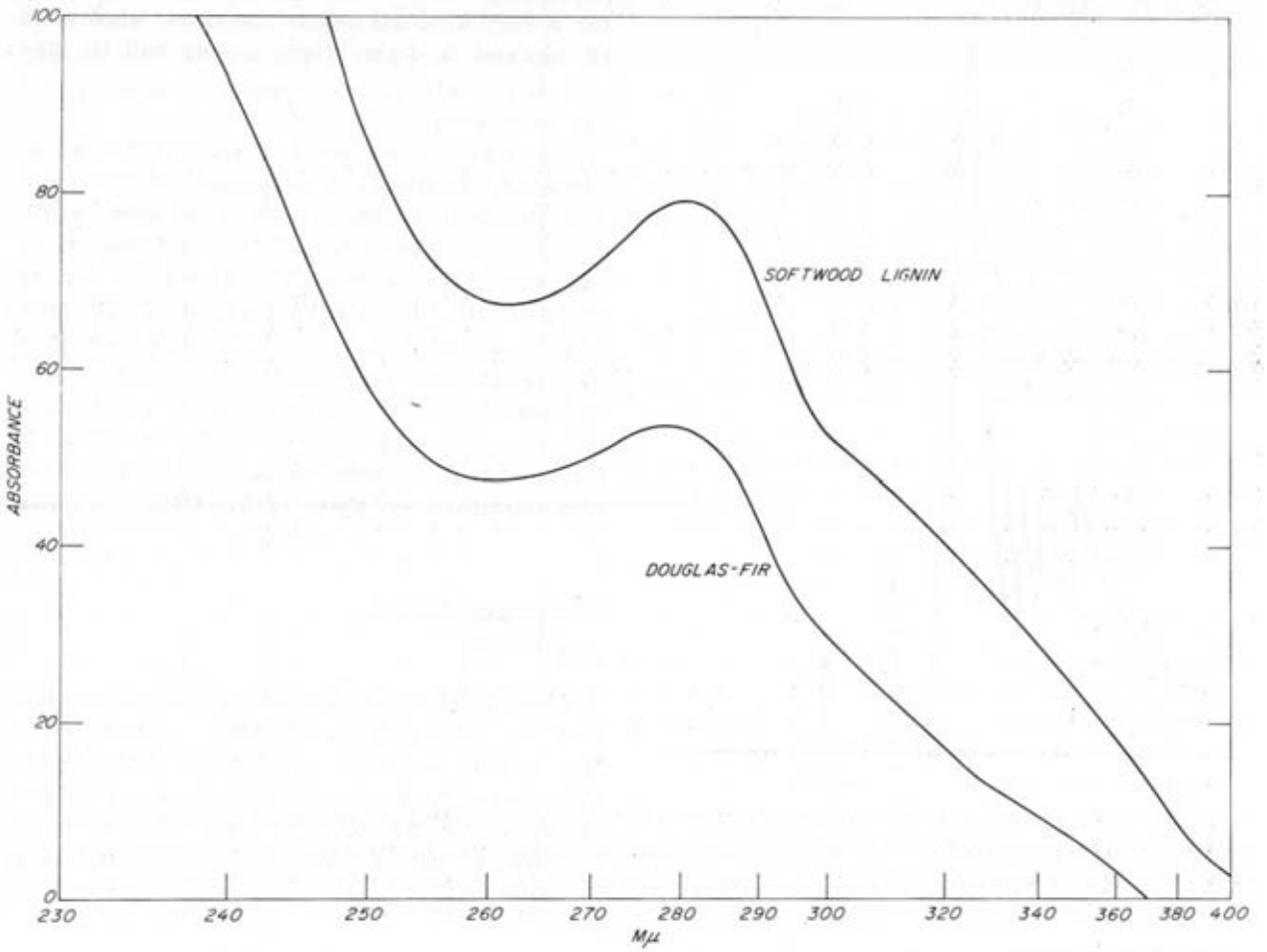


Figure 6.--Ultraviolet absorption spectra of Douglas-fir and softwood lignin.

plotted for comparison and is noted to be quite similar to that of Douglas-fir.

It is known that compared to lignin, cellulose is a weak absorber of ultraviolet light. Therefore, it can be concluded that the absorption of ultraviolet light by wood is largely due to the absorption by lignin.

When light is absorbed by a molecule, it may reemit a part or all of the energy as radiation. It may be immediate (fluorescence) or delayed (phosphorescence). It is known that cellulose exhibits fluorescence (36). It is also known (and used in ultraviolet microscopy) that wood fluoresces. Therefore, it is obvious that wood dissipates a portion of light energy, although the details of these processes are not well defined and should receive some attention.

When a molecule absorbs light energy, it is said to be in an excited state and it may be more reactive, This energy can also be transferred to another molecule as when two molecules of different energy levels collide; in large molecules energy transfer can occur between parts of the molecule, It is not known to what extent, and between which portions of the wood substance, energy transfer takes place, In view of the high absorption of light by the lignin portion of wood (in contrast to cellulose) and the degradation of wood in its entirety, it is most likely that some type of energy transfer from lignin to cellulose and other wood components takes place. This is a problem area worthy of further exploration. It appears possible that lignin acts as a photosensitizer in the degradation of the other wood components.

Free Radicals in Wood

If the energy level of the excited molecule is

sufficiently high, it may dissociate, forming simpler molecules. atoms, or free radicals (reactive fragments having an unpaired electron). Frequently these products react further with each other, or with other substances present. Other work at this Laboratory (16) has shown by electron spin resonance (ESR). spectroscopy that light indeed created free radicals in wood. It was also observed that wood that had been stared in the dark did not contain free radicals in measurable concentrations. Exposure of wood to normal laboratory illumination for a few days produced free radicals in wood in sufficient concentrations for detection with ESR apparatus, The free radicals that were produced in wood by irradiation with ultraviolet light were stable in an inert atmosphere (helium), but in the presence of oxygen disappeared fairly rapidly. Oxygen apparently acted as a radical scavenger in the post-irradiation oxidation reactions that occurred in wood.

The generation of free radicals in wood by gamma rays bas been reported (26). It cannot, however, be assumed that the radicals created by gamma radiation are chemically the same as those caused by light. Because of the high energy of the gamma rays, it is likely that a variety of free radicals are produced in wood in a random fashion, while light probably creates radicals at or near the specific absorbing functional groups in the complicated chemical structure of wood. Comparison of ESR spectra of gamma-irradiated cellulose, wood, and various lignins did not permit identification of the radicals as those belongingto a particular wood component.

It is not known whether. or to what extent the free radicals that were formed by irradiation with light initially contained oxygen. However, from observation of the decay of free radicals in the ESR study (16) it was evident that light-produced radicals react with oxygen. It is therefore likely that peroxides. hydroperoxides, peroxyl, and alkoxyl radicals are among the intermediate products formed. The peroxide concentration in irradiated wood was not measured, as Kleinert (17) did for cellulose. These oxygen-containing intermediates are subject to further chemical and photochemical reactions. because of their low activation energies. Alkoxyl radicals (RO·) are known to be intermediate products of pyrolytic and photolytic reactions of organic peroxides, eaters, ethers, and in autoxidations and in combustion. The reactions of alkoxyl radicals were recently reviewed (15, 35). The products of some of these reactions are identical to those obtained by photodegradation of wood. Therefore, it appears likely that some of these reactions are a part of the photo-oxidation process in wood. Consider, for example,

(1) decomposition

$$RCH_2O\cdot \longrightarrow H\cdot + RCHO$$

$$RCH_2O\cdot \longrightarrow R\cdot + CH_2O$$

(2) hydrogen abstraction

$$RO\cdot + RH \longrightarrow ROH + R\cdot$$

(3) disproportionation

$$2CH_3O\cdot \longrightarrow CH_3OH + CH_2O$$

followed by abstraction of hydrogen from formaldehyde:

$$CH_3O\cdot + CH_2O \longrightarrow CH_3OH + CO$$

(4) addition to other radicals

$$CH_3O\cdot + CH_3\cdot \longrightarrow CH_3OCH_3$$

$$CH_3O\cdot + H\cdot \longrightarrow CH_3OH$$

$$H\cdot + H\cdot \longrightarrow H_2$$

In this manner, through alkoxyl radical intermediates, the formation of methanol, formaldehyde, carbon monoxide, and hydrogen can be explained. These products are among those obtained in the present. study of the photodegradation of wood.

Carbon monoxide may also be formed directly from carbonyl groups by photoelimination. Numerous such reactions are known in the photochemistry of carbonyl compounds. For example, acetone forms carbon monoxide and methyl radicals:

$$CH_3COCH_3 \longrightarrow CO + 2\ CH_3\cdot$$

Carbon dioxide may be formed by way of carboxylic acid groups. Evidence of the formation of carboxyls in wood by irradiation is mentioned later.

In addition to the reactions previously mentioned, methanol could also originate from the numerous methoxyl groups in lignin. The decrease in methoxyl content together with the production of methanol suggests this possibility.

Formation of Volatile Degradation Products

In preliminary work it was observed that volatile decomposition products were formed when yellow-poplar and Douglas-fir veneer samples were irradiated with ultraviolet light. The quantities of gaseous products were convenient to measure and these determinations were developed into a method for studying the significance of irradiation conditions, and other variables.

Yellow-poplar.--Yellow-poplar veneer (0.2 millimeters thick) was dried for 15 minutes at 100° C. It was then irradiated in an air atmosphere for 312 hours with a 2537 A ultraviolet light. The veneer was dried as before and weighed immediately. A weight loss of 0.92 gram was noted (initial weight 5.04 grams, final weight 4.12 grams). The degradation products were collected at intervals during the period of irradiation, and the quantities are given in

Table 6.--Volatile products from yellow-poplar veneer irradiated with a 2537 A light

Time	Millimoles, total				
	CO_2	H_2	CO	H_2O	CH_3OH
Hours					
73.5	3.75	0.55	2.18	----	----
94.5	4.99	.70	2.97	----	----
121.0	6.55	.85	3.90	----	----
144.0	7.97	.90	4.79	----	----
168.5	9.46	1.00	5.72	----	----
191.5	11.01	1.35	6.72	----	----
259.0	15.75	1.70	9.66	----	----
312.0	19.13	1.90	11.77	38	0.78

Figure 7.--The formation of volatile products from yellow-poplar veneer.

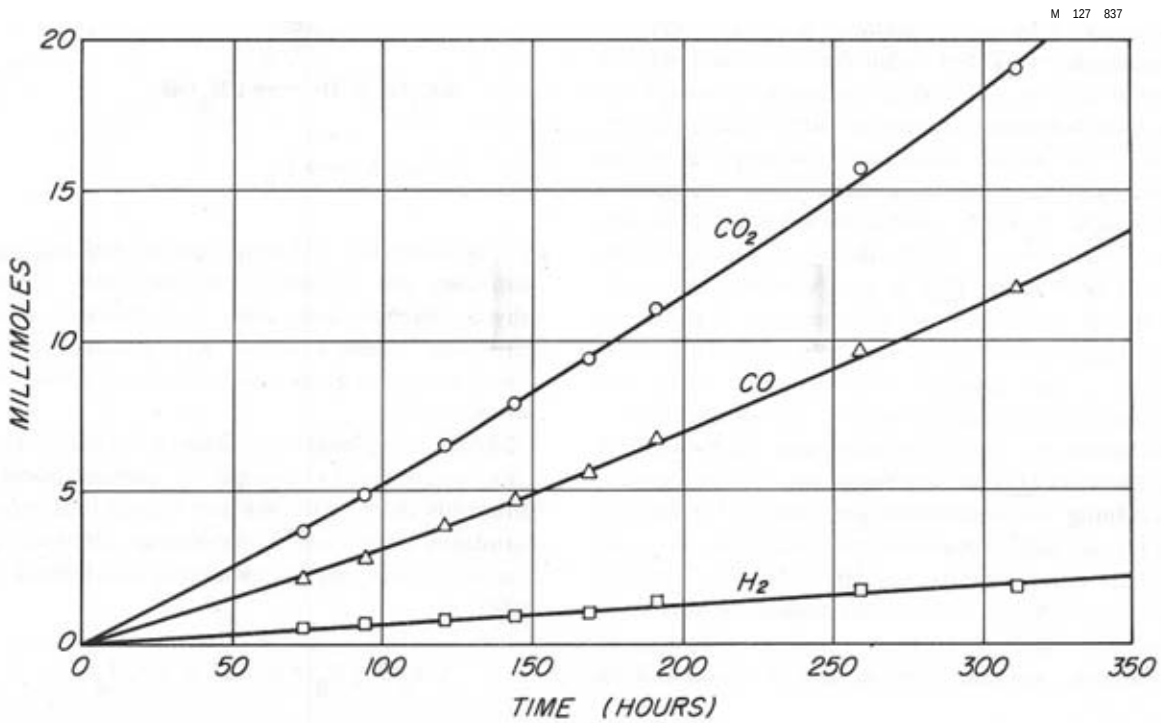


table 6 and figure 7. Final analysis revealed the following:

	Gram
Water	0.689
Methanol	.025
Carbon dioxide	.838
Carbon monoxide	.330
Hydrogen	.004
Total weight of collected products	1.886

It was evident that photo-oxidation had occurred. The total weight of the degradation products actually exceeded the measured weight loss of the veneer. The excess weight of the products is evidently due to a gain of oxygen as is shown by the changes in the weight ratios of the elements in the products:

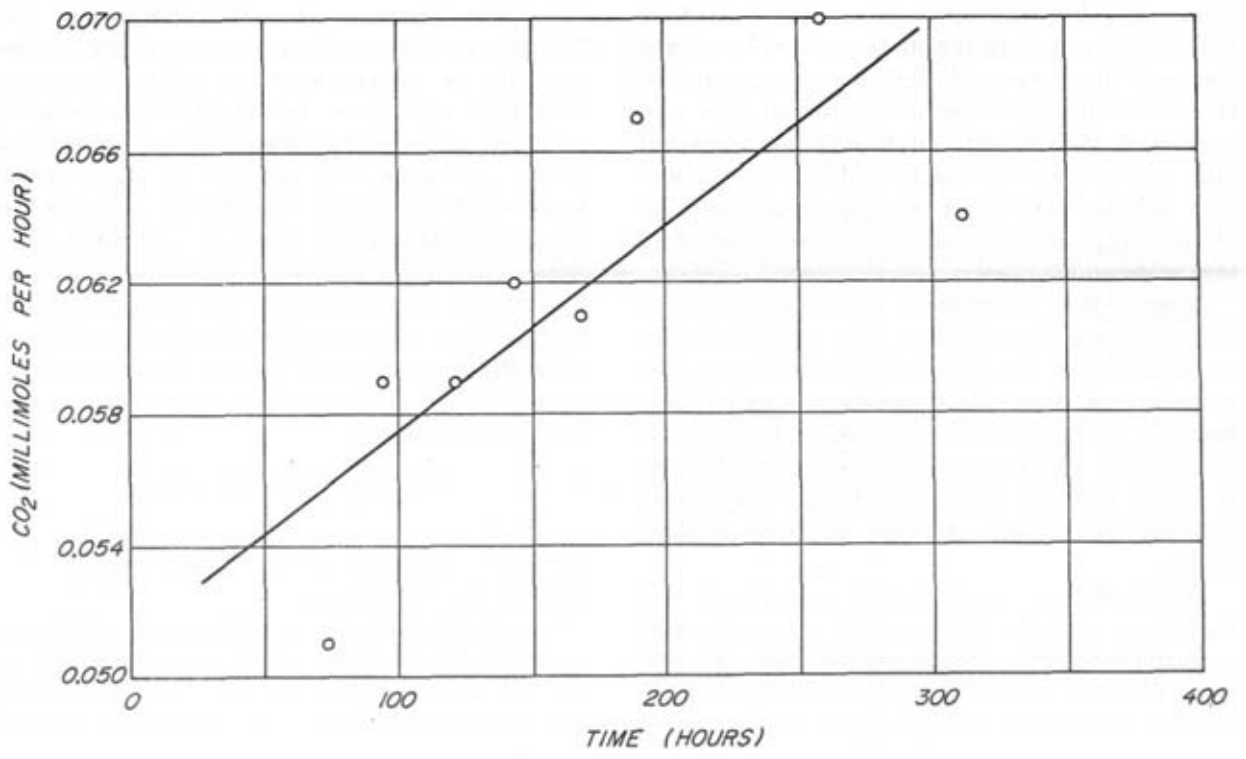
	Percent		
	C	H	O
In wood (4, p. 74)	50	6	44
In products	20	5	75

An examination of figure 7 shows that the rate of gas formation increased with time of irradiation. The increased rate is particularly apparent for carbon dioxide. Figure 8 illustrates the increasing rate of carbon dioxide formation; the quantity of carbon dioxide formed per hour of irradiation for each time interval $\left(\frac{\Delta C}{\Delta t}\right)$ is plotted against time. Carbon dioxide was considered the most reliable indicator of photodegradation in this and in succeeding experiments because it was the most abundant product.

The effect of irradiation on the microstructure

Figure 8.--Change in rate of carbon dioxide formation during irradiation of yellow-poplar veneer.

M 130 250



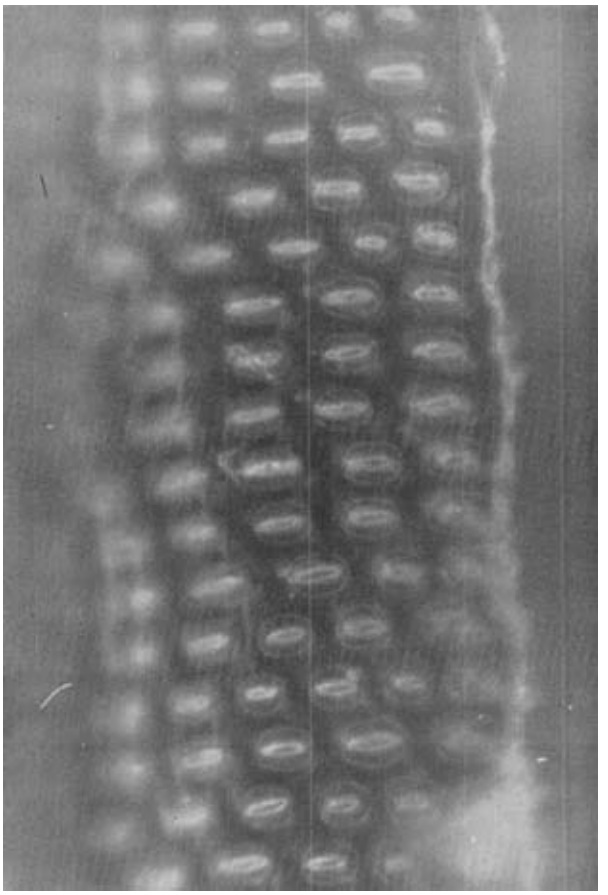


Figure 9.--Photomicrograph of yellow-poplar bordered pits in vessel wall before irradiation (1100X).

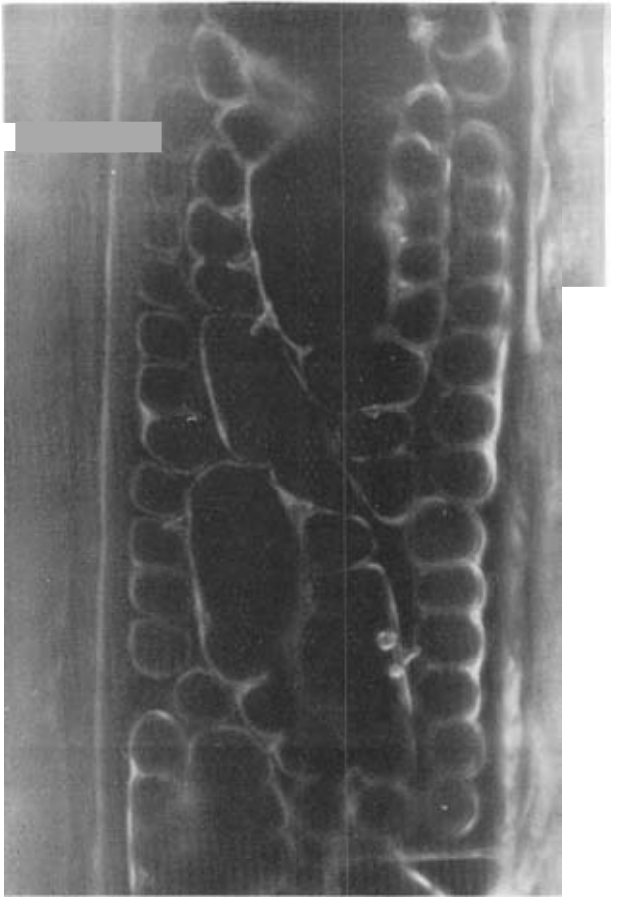


Figure 10.--Photomicrograph of yellow-poplar vessel wall after 2 weeks of irradiation with a 2537 A light (1100X).

of the wood surface was also examined. Figure 9 shows the bordered pits in a vessel wall of yellow-poplar before irradiation. After 2 weeks of exposure to ultraviolet light a large portion of the cell wall including the bordered pits was destroyed (figure 10); no undamaged bordered pits are visible. Such surface effects of irradiation and weathering have been reported by Miniutti (21) and are currently being studied by him in detail.

Douglas-fir. --Douglas-fir veneer was irradiated in vacuum for 56 hours with a 2537 A ultraviolet light. The Srinivasan-Griffin Photochemical Reactor was used. The pressure was maintained between 0.01 and 0.05 millimeters of mercury for several hours before and during irradiation. A liquid nitrogen cooled cold trap was placed between the veneer sample and the vacuum pump.

The condensate in the cold trap (about 0.2 milliliter) and the gas sample above it were analyzed and carbon dioxide, water, and methanol were present. Formaldehyde was not detected. Carbon monoxide and hydrogen are not condensed at the temperature of liquid nitrogen, and their presence was not established. The volatile products were removed promptly from the site of irradiation, and it was therefore concluded that these substances were primary products of wood photodegradation. At atmospheric pressure. the primary products would have remained in the irradiation chamber fox an appreciable length of time and might have been converted to secondary products, or further, This might have been the case when irradiation was carried out in an air atmosphere and formaldehyde was detected among the degradation products. Formaldehyde is known to be a photoproduct of methanol:

$$CH_3OH \longrightarrow CH_2O + H_2$$

However, with the 2537 A light source, this reaction is very slow.

The observation that carbon dioxide and water were produced when wood was irradiated in vacuum suggests that chemical rearrangements have occurred in wood. Carboxyl groups in wood

probably do not account for the formation of all the carbon dioxide and water. The same conclusion applies for the results of irradiation in an inert atmosphere as will be described later.

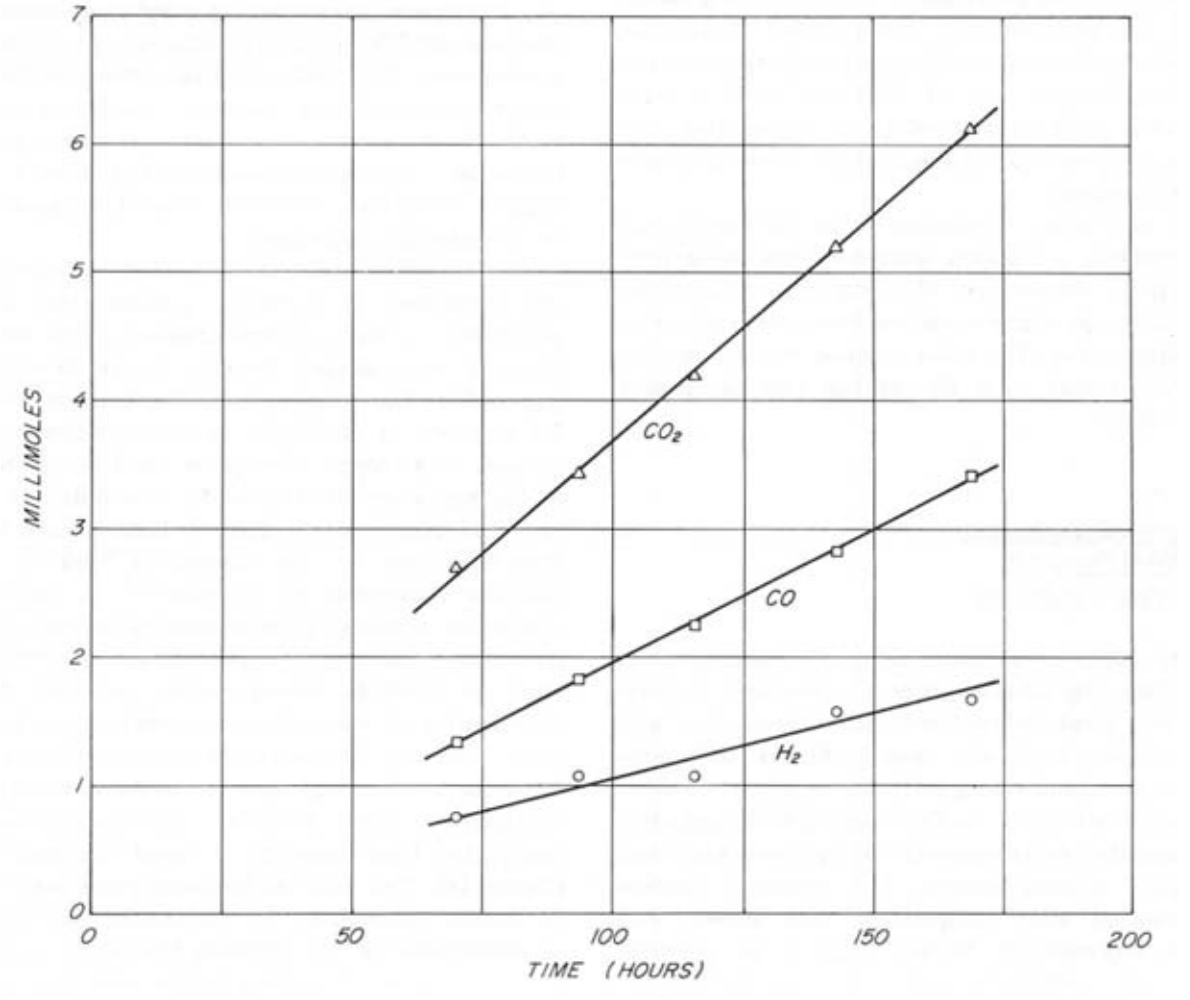
Douglas-fir veneer (0.25 millimeters thick) was also irradiated in an air atmosphere for 168 hours with the 2537 A germicidal lamp. The principal degradation products were carbon dioxide, carbon monoxide, water, hydrogen, and methanol (table 7 and figure 11). Small quantities of formaldehyde and acetic and/or formic acid were also obtained. Carbon monoxide and dioxide were formed approximately at a constant rate.

Table 7.--Volatile products from Douglas-fir veneer

Irradiation time	Millimoles, total		
	CO_2	H_2	CO
Hours			
70	2.70	0.76	1.34
93	3.42	1.08	1.82
116	4.20	1.08	2.26
143	5.20	1.57	2.92
168	6.12	1.68	3.41

In figure 11 the quantities of gases collected are plotted against the time of irradiation. Essentially straight lines were obtained, but the significance

Figure 11.--The formation of volatile products from Douglas-fir veneer irradiated with a 2537 A light in an air atmosphere.



of this observation is not entirely clear. Several explanations for the constant rate are possible.

Degradation rate.--In photochemical reactions the rate of activation of molecules is known to be proportional to the intensity of absorbed light. In these experiments the incident light was approximately constant, as the intensity of the light source is known to change very little with time. It was observed that the rate of formation of carbon dioxide from Douglas-fir was constant over the period of time investigated. This suggests that the intensity of the absorbed light was constant, indicating that the ultraviolet light absorption characteristics of Douglas-fir did not change materially during irradiation.

The yellow-poplar veneer was irradiated for a longer period of time, and an increasing rate of degradation product formation was observed. It is possible that in this case the absorption characteristics changed with the time of irradiation, and that as a result, the intensity of the absorbed light increased. It also seems possible that the efficiency of some energy dissipation process decreased during the irradiation, thereby increasing the rate of degradation. It is conceivable that some product of degradation acts as a photosensitizer, which accelerates the breakdown process.

In any case, a constant or an increasing rate of product formation suggests that essentially complete conversion of wood into volatile degradation products occurred. Incomplete reaction, leaving unreactive wood residue on the surface should result in a decreasing rate of product formation.

Chemical Changes in Wood Resulting From Irradiation

In addition to measuring the quantities of volatile degradation products, chemical analysis of the wood before and after irradiation with ultraviolet light was used to follow the breakdown process. Changes in the methoxyl content, ethanol solubility, and pH were determined after irradiation of Douglas-fir or yellow-poplar with a 2537 A light source, The methoxyl content decreased after irradiation. This agrees with data reported by Forman (12). It is possible that the methanol found among the degradation products was derived from the methoxyl groups. The quantity of methanol that was collected corresponded to about half of the methoxyl groups that were lost. A decrease in the pH was also noted. These changes are listed in table 8.

Table 8.--Chemical changes in Douglas-fir ground wood irradiated with a 2537 A light

Exposure	pH	Methoxyl	Ethanol solubility
		Pct.	Pct.
Before irradiation	3.7	5.1	4.1
Irradiated for 168 hours in air	3.0	4.8	---
Irradiated for 168 hours in nitrogen	3.7	4.9	---
Irradiated for 456 hours in nitrogen	3.4	4.9	3.1
Irradiated for 330 hours in air	2.7	4.9	5.2

The solubility in ethanol increased as a result of irradiation in an air atmosphere, while a decrease was noted after irradiation in a nitrogen atmosphere. This indicated that under conditions where oxidation was possible, wood was converted to some extent into ethanol-soluble products. In a nitrogen atmosphere a portion of the soluble materials was made insoluble, possibly by crosslinking reactions,

The decrease in pH after irradiation indicated the formation of carboxyl groups. This was confirmed by infrared spectroscopy. The spectrum of unirradiated Douglas-fir is shown in figure 12. The weak absorption band at about 5.8 microns is attributed to carbonyl functional groups. A stronger absorption band is apparent in the spectrum of Douglas-fir irradiated in an air atmosphere with a 2537 A Light (figure 13). This increase of the absorption band at 5.8 microns represents an increase in the concentration of carbonyl groups, without distinguishing between the various types of carbonyl groups, such as aldehyde, ketone, ester, and acid. The contribution of the carboxylic acid groups, however, can be demonstrated by neutralization. Then the carboxyl groups are in the form of the carboxylate anion (RCOO-) and the infrared absorption band appears at about 6.2 microns (figure 14). The shift of the absorption band can be shown numerically by calculating the ratios of absorbance at 5.8 microns (carbonyl) and at 6.2 microns (carboxylate) to the absorbance at

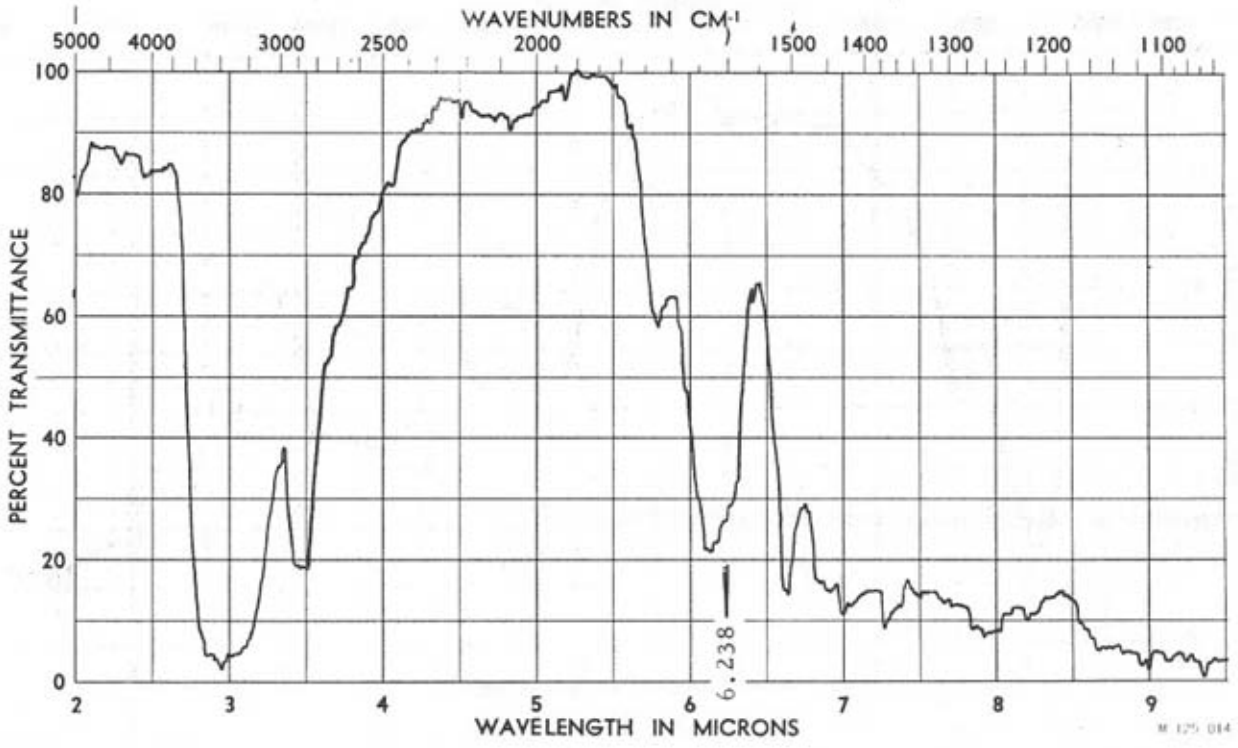
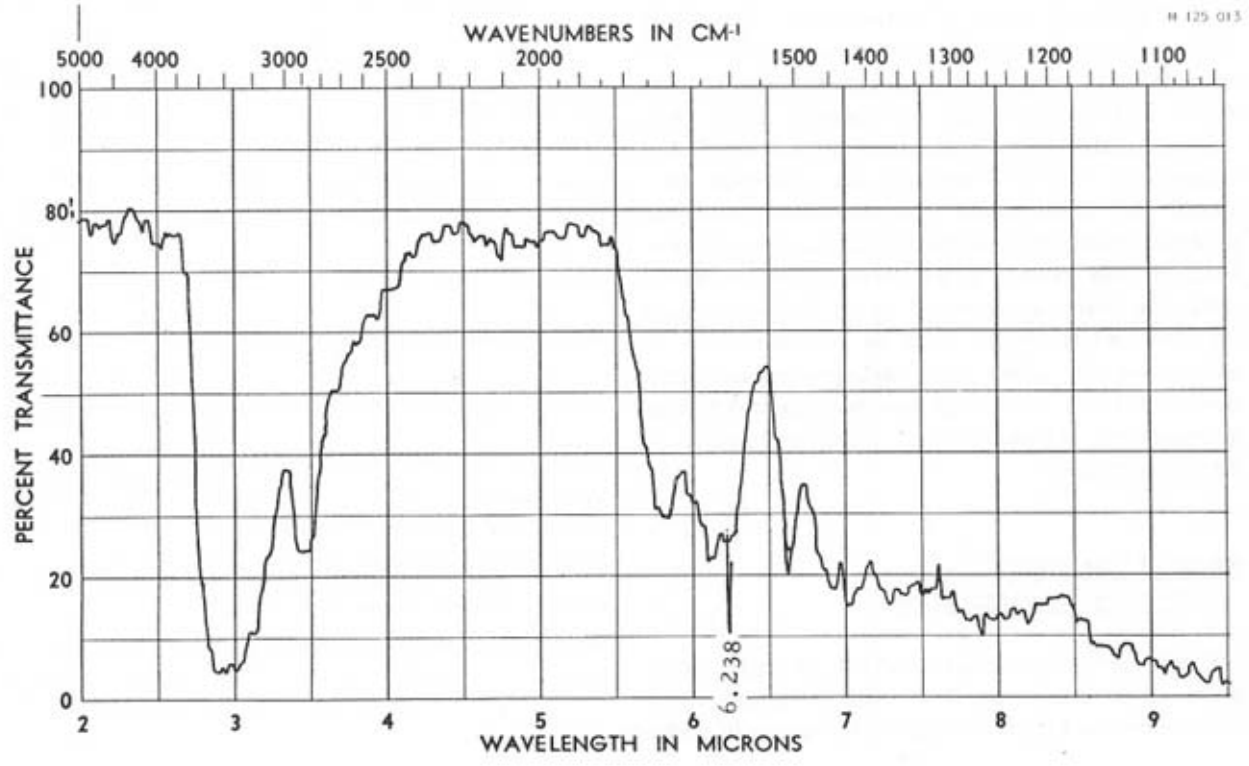


Figure 12.--Infrared spectrum of Douglas-fir ground wood before irradiation.

Figure 13.--Infrared spectrum of Douglas-fir ground wood after irradiation in air with a 2537 A light.



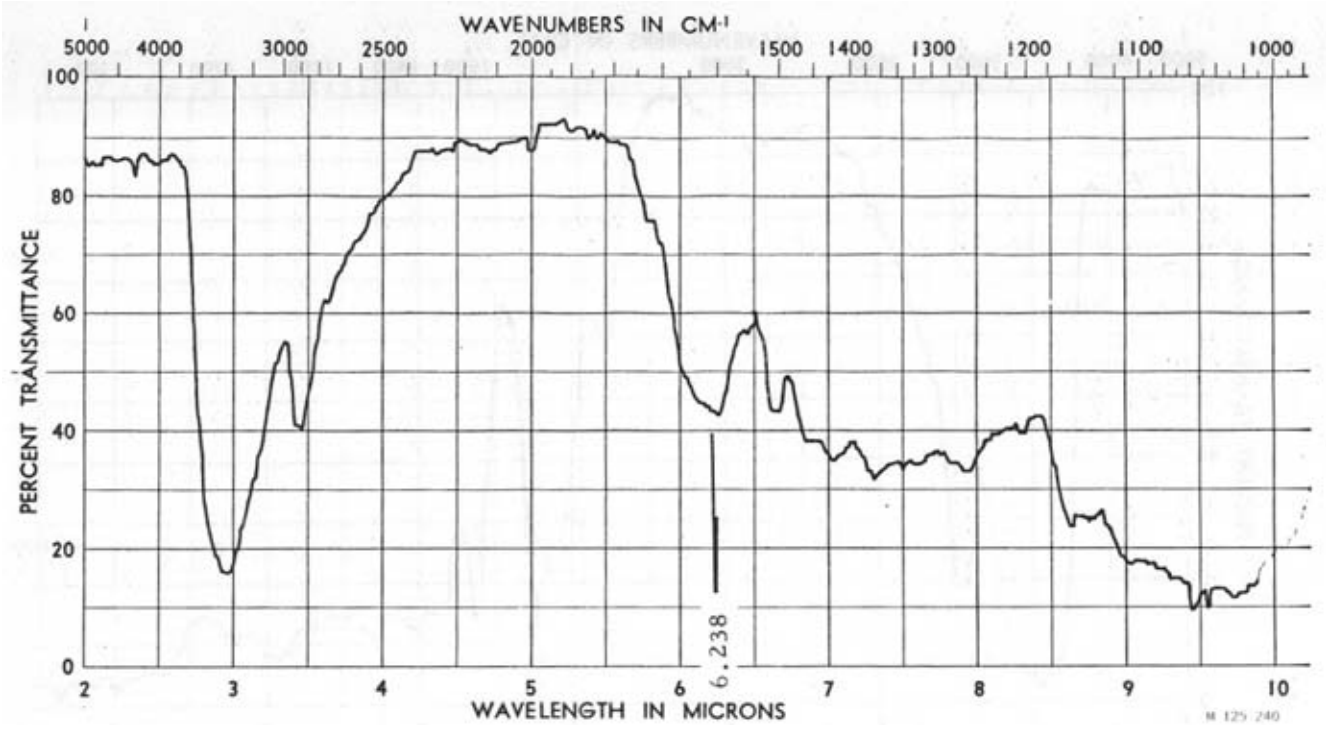


Figure 14.--Infrared spectrum of Douglas-fir ground wood irradiated in air and neutralized with sodium hydroxide.

about 6.8 microns, which apparently remains unchanged (table 3).

To eliminate possible interference by extractives, hot-water-extracted yellow-poplar veneer was used in a similar experiment. The same light source was used, and irradiation in an air atmosphere was continued for 96 hours. The ratios were calculated as before (table 10).

It is evident that a significant increase in the number of carbonyl groups has occurred as a result of irradiation. The decrease following neutralization represents the proportion of carboxylic acid groups in the total. After acidification, the carbonyl concentration did not regain the maximum level. This is probable due to extraction of some carboxyl-group-containing material from wood that has become soluble as a result of irradiation or possibly because of decarboxylation.

Table 9.--Carbonyl and carboxyl concentration in Douglas-fir wood

Exposure and treatment	Relative absorbance	
	5.8 microns	6.2 microns
Unexposed Douglas-fir	0.27	0.82
After irradiation in air (330 hours)	.65	.83
After irradiation and neutralization	.22	.89

Table 10.--Carbonyl and carboxyl concentration In yellow-poplar

Exposure and treatment	Relative absorbance	
	5.8 microns	6.2 microns
Yellow-poplar before irradiation	0.70	0.65
After irradiation in air (96 hours)	.97	.67
After irradiation and neutralization	.78	.73
After acidification with dilute HCl	.71	.59

Effect of Wavelength and Oxygen Concentrations

When the detrimental action of light on a material is examined it is usually necessary to determine the effect of oxygen. If oxygen is with-

out effect on the degradation process, then photolysis or photochemical bond scission is suspected. If oxygen affects the rate of degradation, or its nature, or the types of products, then photo-oxidation or other participation of oxygen is indicated.

Preliminary investigations of the formation of volatile products in an air atmosphere indicated that oxygen entered into the photodegradation process and was included in the products. We sought then to discover to what degree oxygen contributed to the degradation of wood by irradiating yellow-poplar veneer specimens in the absence of oxygen (nitrogen) and in air. The wavelength of irradiation proved to be interrelated and is also discussed. The effect of an atmosphere of pure oxygen was also examined in irradiations of Douglas-fir veneer.

The susceptibility of organic materials to the effects of light varies with the wavelength and the absorption characteristics of the material being irradiated. It is necessary that light is absorbed, and that the energy per quantum is sufficiently high for a chemical change to occur. The lowest energy effective in producing chemical changes is known as the threshold energy. A thorough study of the significance of the complete spectrum of wavelengths for a material like wood would be a major undertaking and was not attempted in this study. It was possible, however, to show some marked differences in the degradation of wood by two ultraviolet light sources of different characteristics; one had a peak intensity at 3500 A, and the other source emitted principally the 2537 A wavelength. These data along with the effects of oxidizing and inert atmospheres are shown in table 11.

Table 11.--Products of degradation of yellow-poplar in air and nitrogen atmospheres by light sources of two different wave length characteristics

Atmosphere and light source		Millimoles, total after 168 hours						pH[1]
		CO_2	CO	H_2	CH_3OH	CH_2O	H_2O	
Air	2537 A	3.69	2.46	0.53	0.08	0.13	6.88	3.47
	3500 A (peak)	1.41	1.03	None	.09	.05	4.22	3.16
Nitrogen	2537 A	.18	.31	.01	Trace	None	Trace	4.22
	3500 A (peak)	None	None	None	Trace	None	Trace	4.19

[1]The pH of unirradiated wood was 3.78.

Air and nitrogen.--The data show that after irradiation for 168 hours in air the shorter wavelength of 2537 A produced significantly greater quantities of all volatile degradation products than the longer wavelength of 3500 A. When these quantities are corrected to reflect the effect of the two light sources compared at equal intensities, the shorter wavelength still was more effective in producing degradation (figure 15).

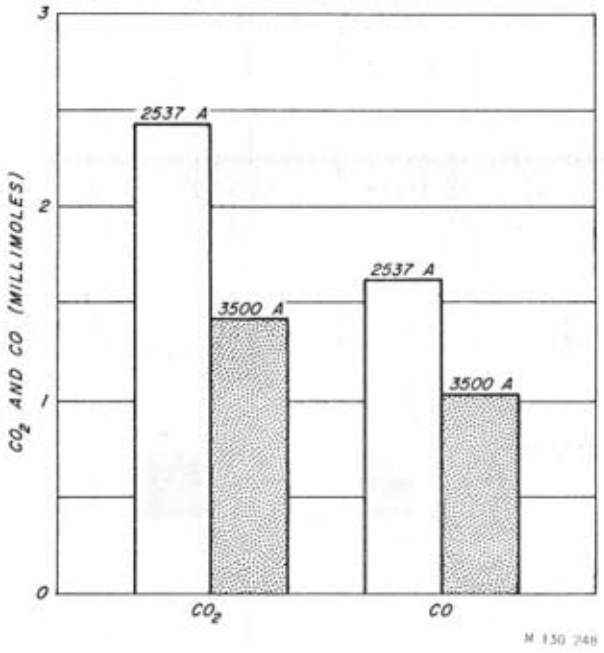


Figure 15.--Comparison of quantities of carbon dioxide and carbon monoxide produced from yellow-poplar by irradiation with 2537 A and 3500 A lights of equal intensities.

In a nitrogen atmosphere, the amount of carbon dioxide that was formed by irradiation with the 2537 A light was only one-twentieth of that obtained during irradiation in an air atmosphere (figure 16). Similarly, the amount of carbon monoxide that was formed was reduced in the nitrogen atmosphere by a factor of about 8. After irradiation in nitrogen with the longer wavelength (3500 A) no measurable quantities of volatile products were found (table 11), and only traces of methanol and water were detected.

A comparison of data for an inert atmosphere (nitrogen) and an air atmosphere showed that photo-oxidation was largely responsible for the formation of volatile products during irradiation of wood, The formation of smaller quantities of

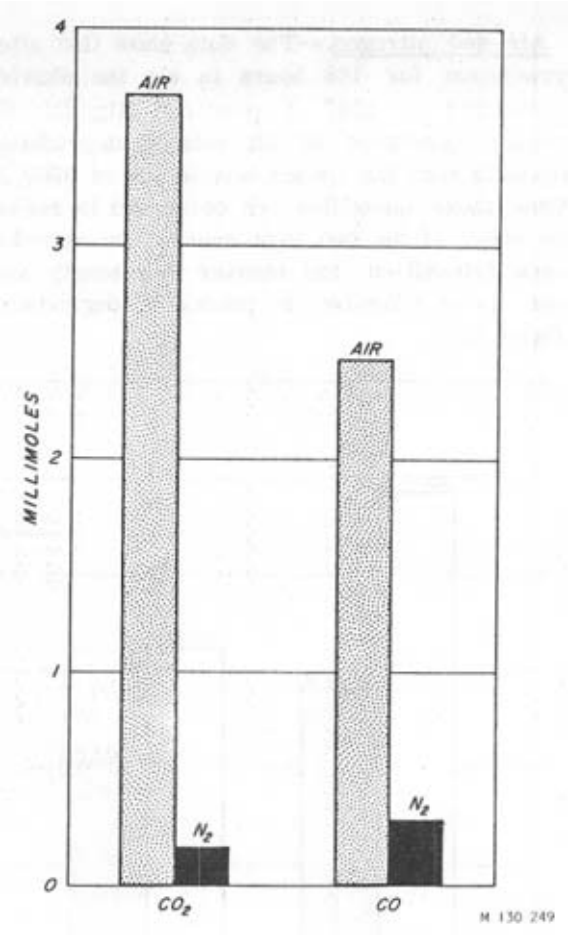


Figure 16.--Comparison of quantities of carbon dioxide and carbon monoxide as photodegradation products from yellow-poplar veneer irradiated in air and nitrogen atmospheres with a 2537 A light.

most of the products in the absence of oxygen at 2537 A indicated the existence of another degradation mechanism in addition to photo-oxidation. At longer wavelengths of about 3500 A the degradation products were produced only by photo-oxidation but at a slower rate than by the shorter wavelength. More research is needed to establish the threshold wavelength effective in causing oxidation of wood.

It is seen that photo-oxidation is an important mechanism of wood degradation by 2537 A ultraviolet light. It is interesting to note that this result is in contrast to the degradation of pure cellulose (18) by the same wavelength where oxygen was reported to have no effect. This presumably reflects the role of lignin in the photo-oxidation of wood. Apparently lignin acts as a photosensitizer for cellulose oxidation although lignin itself is degraded as well.

Photolytic (nonoxidative) production of simple degradation products, was observed only in the middle ultraviolet (2537 A), It would be of considerable technological as well as fundamental interest to know the threshold wavelength for this degradation process and if it lies in the ultraviolet region of sunlight that strikes the earth's surface.

Pure oxygen.--Having established that oxygen was an important factor in the photodegradation of wood, it was of interest to determine if the rates of formation of volatile degradation products were further increased by irradiating wood in an atmosphere of pure oxygen There was some speculation that carbon monoxide found in previous experiments resulted from incomplete oxidation. The results of the irradiation of Douglas-fir veneer with the 2537 A light in atmospheres of nitrogen, air, and oxygen are shown in table 12 and figure 17.

Table 12.--Products of degradation of Douglas-fir veneer irradiated with a 2537 A light under Three levels of oxygen concentration

Atmosphere	Millimoles, total after 168 hours		
	CO_2	CO	CO_2/CO
100 percent oxygen	8.76	4.90	1.8
Air (20 percent oxygen)	6.12	3.41	1.8
Nitrogen (0 percent oxygen)	1.07	1.04	1.03

In a nitrogen atmosphere carbon monoxide and dioxide were formed at a very slow rate. An increase in the rate was observed when air was used during irradiation, and a further gain was recorded with an atmosphere of oxygen. However, the ratio of the quality of carbon dioxide to carbon monoxide formed in atmospheres of air and oxygen remained at ehe same value of 1.8. This indicated that carbon monoxide was a legitimate photo-oxidation product and not the result of incomplete oxidation.

Effect of Temperature

Temperature often accelerates reaction rates.

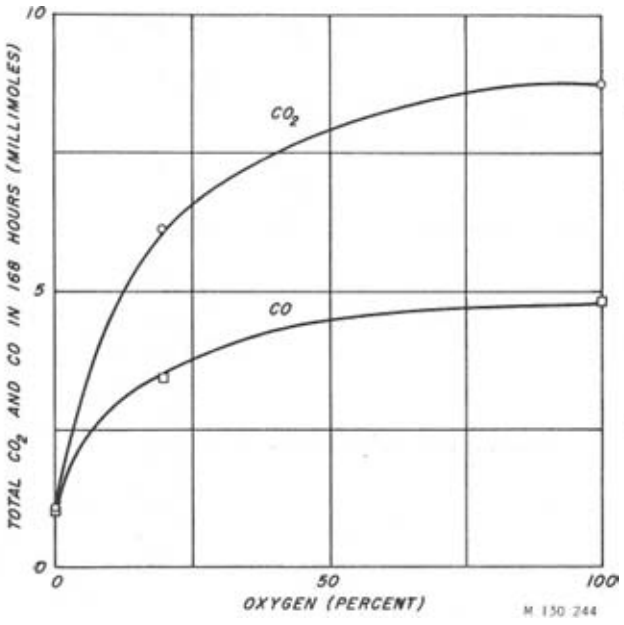


Figure 17.--Effect of oxygen concentration on formation of carbon dioxide and carbon monoxide during irradiation of Douglas-fir veneer.

In thermal reactions a 10°C. increase in temperature frequently results in a twofold ox threefold increase in the rate. Primary photochemical reactions are notable exceptions to this general rule. Temperature coefficients near unity are common for these reactions. Secondary reactions in photochemical processes are usually influenced by temperature, but when free radicals are involved, a small temperature coefficient for the overall process usually results, This is because the temperature coefficient is determined by the activation energy, and for free radicals this energy is usually very small or is zero.

Therefore, knowledge of the influence of temperature on reaction rates can be helpful in interpreting reaction mechanism. In this study, it is evident from the results that temperature had little effect on reaction rate, There was in fact a small negative temperature coefficient for most products (table 13 and figure 18). From these observations it might be concluded that, at 2537 A, CO and CO_2 are products of either primary photochemical reactions or more likely, of free radical reactions, and therefore fail to show the effect of temperature differences on the reaction rates. There is at least one other possible explanation. The rates of reactions forming CO and

Table 13.--Products of degradation of yellow-poplar veneer at 55° and 90° C. irradiated with a 2537 A light

Temperature	Atmosphere	Millimoles, total after 168 hours					pH	Relative carbonyl concentration
		CO_2	CO	H_2	CH_3OH	CH_2O		
°C.								
55	Air	3.69	2.46	0.53	0.08	0.13	3.47	1.15
90	Air	2.77	1.91	.32	.32	Trace	3.28	1.12
55	Nitrogen	.18	.31	.01	Trace	None	4.22	.79
90	Nitrogen	.13	.32	.93	Trace	None	4.34	.79
Unexposed wood	----	----	----	----	----	----	3.78	.67

CO_2 could be temperature dependent and still fail to show it in these experiments if the rate-controlling step were the photochemical activation of wood. This could possibly occur if low light intensities were used, or if the material were relatively unreactive photochemically. In the case of an excellent absorber of ultraviolet light, such as wood, inefficient photochemical activation of wood suggests a highly efficient energy dissipation by fluorescence, phosphorescence, or conversion to heat. According to our estimates, the quantum yields were relatively low. This supports the energy dissipation hypothesis.

The slight negative thermal effect that was observed may also indicate the existence of competing chemical reactions, one of which does not result in the formation of volatile products, and is influenced by temperature. Then at a higher temperature the reaction that does not produce volatile products would be favored, and a decreased rate of volatile product formation would be observed.

The clarification of some of these questions requires further work.

Effect of Humidity

A high moisture content in wood could enable hydrolysis reactions to take place or favor other reactions that proceed by ionic mechanisms. Therefore, the effect of humidity on the photodegradation of wood was investigated.

In this work an atmosphere of about 93 percent relative humidity was obtained by passing air through a saturated solution of sodium sulfate. The quantities of volatile products that were

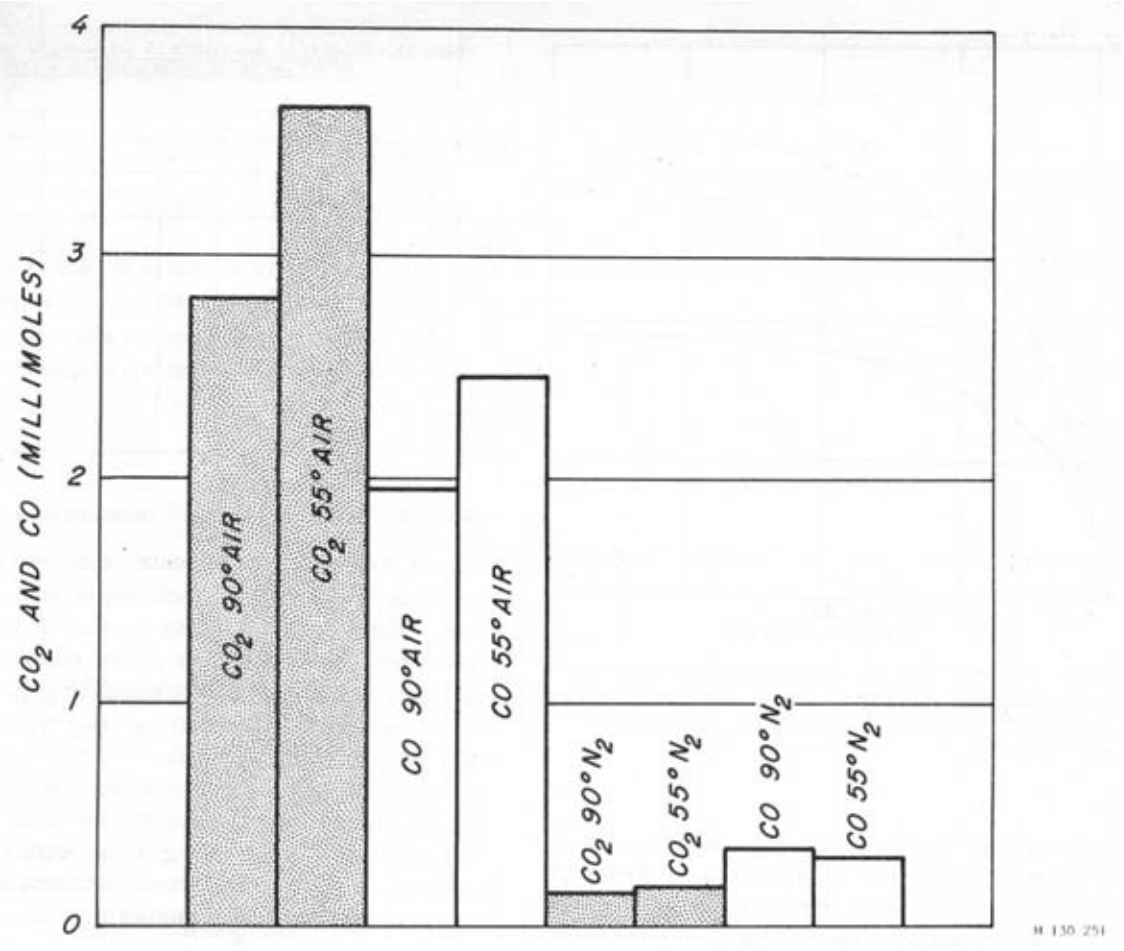


Figure 18.--The effects of 55° and 90° C. temperatures on formation of carbon dioxide and carbon monoxide from yellow-poplar irradiated with a 2537 A light in air and nitrogen.

formed were compared to those obtained when an atmosphere of dry air was used. The light source was a 30 watt blacklight lamp having a peak intensity at about 3650 A. Douglas-fir veneer was used, and the time of irradiation was 168 hours. The results are shown in table 14.

Table 14.--Effect of humidity en photodegradation of Douglas-fir veneer irradiated with a 3650 A light

Humidity	Millimoles, total after 168 hours			
	CO_2	CO	H_2	CH_3OH
Relative humidity > 90 percent	1.64	0.7	0.2	0.30
Dry air	1.15	.87	.05	.18

Somewhat larger quantities of most of the volatile products were obtained with high humidity. This suggests that reactions favored by the presence of moisture are involved in degradation reactions leading to volatile products of decomposition. Additional work is needed to further define the nature and scope of this effect.

Post-Irradiation Effect

The post-irradiation effect is the phenomenon of continued degradation of a material after irradiation has ceased. If there is indeed a post-irradiation effect it would mean that degradation of wood continues under conditions of periodic irradiation, as is the case in nature. It might also indicate that reactive sites or free radicals could be accumulated in wood during irradiation, and later react with oxygen to form volatile degradation products in the absence of light.

In these experiments softwood cellulose and Douglas-fir veneer were irradiated in an inert atmosphere (nitrogen or helium) and then exposed to an oxygen-containing atmosphere without irradiation. The subsequent generation of volatile

degradation products would be positive evidence for the existence of a post-irradiation effect. As was mentioned previously, a post-irradiation effect had been reported in cellulose (34), as indicated by the continuing decrease of the degree of polymerization subsequent to irradiation.

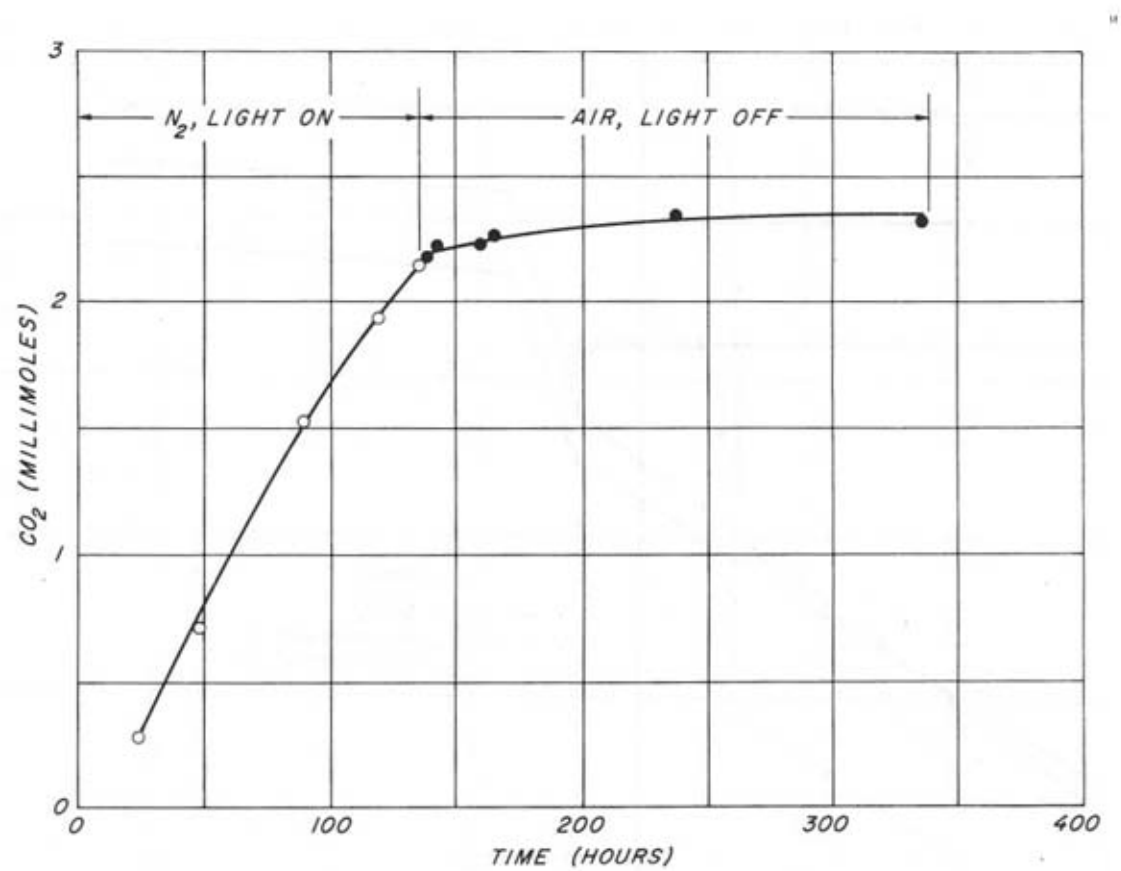
Purified softwood cellulose in sheet form was irradiated with a 2537 A light in a nitrogen atmosphere. When the light was turned off, and air was admitted, no significant formation of volatile degradation products was observed (table 15, figure 19). This indicated that the post-irradiation effect in wood cellulose did not result in the formation of volatile products, or sufficient quantities of the products for detection in our apparatus. Since it is known that the post-irradiation effect exists in cellulose, and results in chain scission, it may mean that chain scission is not linked with immediate formation of CO and CO_2.

The existence of a post-irradiation effect In

Table 15. --Post-irradiation effect in softwood cellulose irradiated with a 2537 A light

Time	Atmosphere	Millimoles total		
		CO_2	H_2	CO
Hours				
0	Nitrogen, light on			
24	.....do.....	0.28	0.30	0.30
48	.....do.....	.71	.68	.77
90	.....do.....	1.52	1.12	1.64
119	.....do.....	1.93	1.48	2.38
136	Light off, air in	2.14	1.41	2.44
139	Air, light off	2.18	1.44	2.47
143	.....do.....	2.22	1.53	2.52
160	.....do.....	2.22	1.52	2.52
166	.....do.....	2.26	1.50	2.55
238	.....do.....	2.34	1.52	2.54
336	.....do.....	2.32	1.61	2.56

Figure 19.--No post-irradiation effect was observed in softwood cellulose. After irradiation ceased little additional carbon dioxide was formed.



wood was indicated in the study of radicals in wood by electron spin resonance spectroscopy (16). It was observed that in helium the radicals were stable over long periods of time, while in air their concentration decreased rapidly. It was not learned in that study, however, whether free radical oxidation yielded volatile degradation products in the absence of further irradiation.

Douglas-fir veneer was irradiated with a 2537 A light in a helium atmosphere. When irradiation ceased, and air or oxygen was admitted, the volatile products were formed at an increased rate. This result indicated that a post-irradiation effect existed in wood and that it resulted in the formation of volatile degradation products (table 16, figure 20).

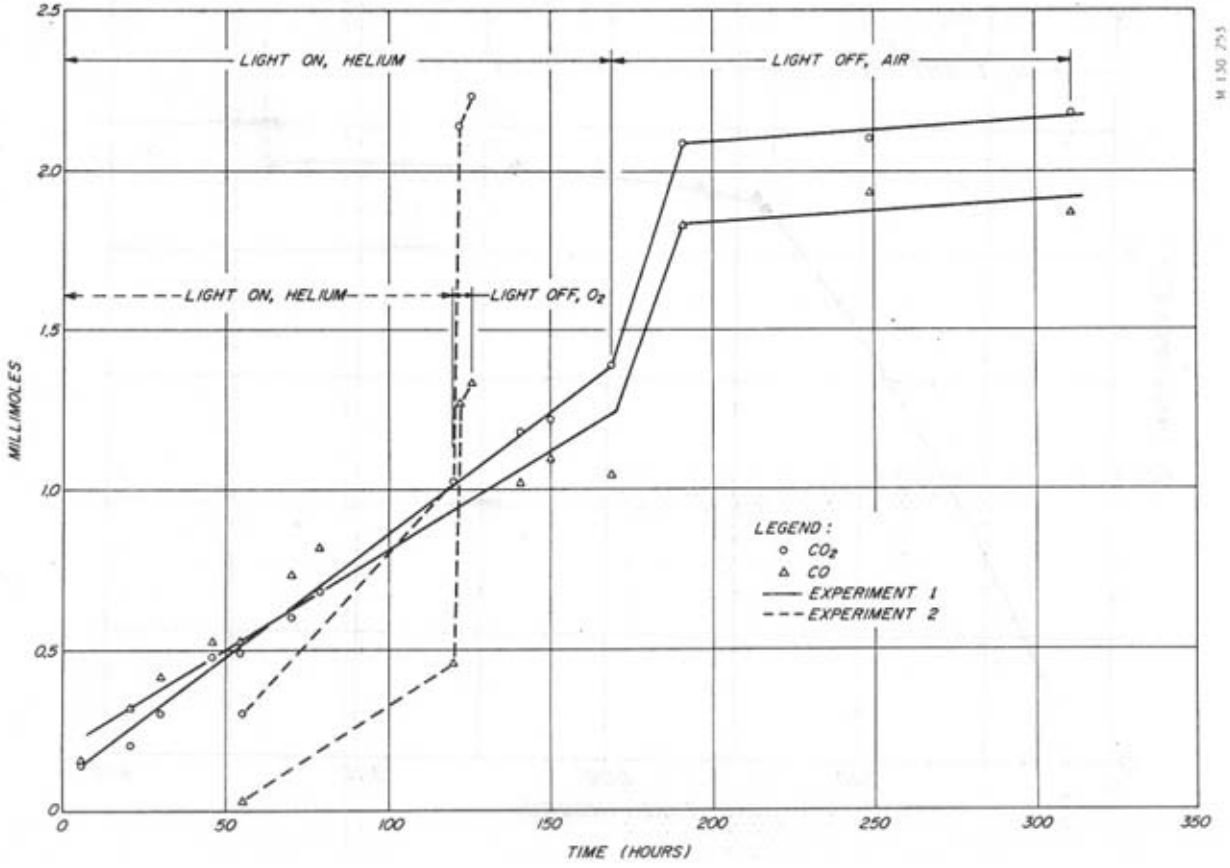
Quantum Yield Estimate for the Formation of Volatile Products

The quantum yield for the formation of irradiation products is a useful indicator of the

Table 16.--Post-irradiation effect in Douglas-fir veneer irradiated with a 2537 A light

Time	Atmosphere	Millimoles total		
		CO_2	H_2	CO
Hours				
0	Helium, light on			
6	.....do.....	0.14	0.11	0.15
22	.....do.....	.20	.16	.32
30	.....do.....	.30	.14	.42
46	.....do.....	.48	.16	.53
54	.....do.....	.49	.27	.53
70	.....do.....	.61	.33	.74
78	.....do.....	.68	.19	.82
142	.....do.....	1.18	.31	1.02
150	.....do.....	1.22	.37	1.10
168	Light off, air in	1.39	.34	1.05
192	.....do.....	2.09	1.73	1.83
248	.....do.....	2.10	1.81	1.93
312	.....do.....	2.18	1.84	1.87
0	Helium, light on			
56	.....do.....	.30	----	.03
120	Light off, oxygen in	1.05	----	.46
123	.....do.....	2.14	.17	1.27
126	.....do.....	2.23	.18	1.34

Figure 20.--Post-irradiation effect in Douglas-fir veneer irradiated with a 2537 A light.



efficiency of the process. It may be defined as the number of molecules of product formed per quantum of light absorbed. In chain reactions the quantum yield is a large number, and in many typical photochemical reactions it is near 1. A direct quantum yield determination for wood is very difficult because of the problem of measuring the amount of light absorbed. The minimum quantum yield can be estimated if the incident intensity is known and if complete absorption is assumed. This could be done in this case using data provided by the manufacturer of the photochemical reactor who reported that 1.65×10^{16} photons of 2537 A ultraviolet and 1.5×10^{16} to 5×10^{16} photons of 3500 A ultraviolet light per second per cubic centimeter are generated. The volume of the reaction chamber was about 400 cubic centimeters. Therefore, the number of photons per hour in the reaction chamber was about 2.4×10^{22} for the 2537 A light source and from 2.2×10^{22} to 7.2×10^{22} for the 3500 A light.

The minimum quantum yield is then given by:

$$\frac{\text{moles of product} \times \text{Avogadro's number}}{\text{hours of irradiation} \times \text{photons per hour}}$$

The minimum quantum yields presented in table 17 were calculated from the data in table 11 (page 45). These values should serve only to establish an approximate lower limit for the quantum yields until accurate values are determined.

Flynn and Morrow have reported (10) that the quantum yields for the formation of hydrogen were 10^{-2} and 10^{-3} for carbon monoxide plus carbon dioxide when cellulose was irradiated in vacuum with 2537 A ultraviolet light. If the results of irradiation are assumed to be the same or similar in a nitrogen atmosphere as in a vacuum, an estimate can be made of the quantum yields for the formation of gaseous products from wood.

For our quantum yield determinations a purified softwood cellulose sheet was irradiated in a nitrogen atmosphere with a 2537 A ultraviolet light. After 48 hours of irradiation, quantities of carbon dioxide, carbon monoxide, and hydrogen were collected and are shown in table 18 along with the quantities of the same gases obtained from Douglas-fir veneer under identical conditions of irradiation.

The approximate quantum yields (ϕ) of volatile products from wood resulting from irradiation in a nitrogen atmosphere were calculated. The reported (10) quantum yields of volatile products

Table 18.--Volatile photodegradation products from purified wood cellulose and Douglas-fir veneer irradiated in nitrogen with a 2537 A light

Material	Millimoles, total after 48 hours		
	CO_2	CO	H_2
Purified wood cellulose	0.7	0.8	0.7
Douglas-fir veneer (Average of four experiments)	.4	.3	.2

Table 17.--Minimum quantum yields of gaseous photodegradation products from yellow-poplar veneer

Light source	Atmosphere	Minimum quantum yield[1]		
		CO_2	CO	CO_2, CO, and H_2
2537 A	Air	5.5×10^{-4}	3.7×10^{-4}	----
2537 A	Nitrogen	----	----	7.5×10^{-5}
3500 A	Air	$.7\text{-}2.3 \times 10^{-4}$	$.5\text{-}1.6 \times 10^{-4}$	----

[1]Number of molecules formed per photon of light absorbed.

from cellulose and the quantities of products that were obtained in these experiments were used in the calculation:

$$\phi \text{ (of volatile products from wood)} = \frac{\phi \text{ (of volatile products from cellulose)} \times \text{millimoles volatile products from wood}}{\text{millimoles of volatile products from cellulose}}$$

$$\text{(a) } \phi\,(CO + CO_2 \text{ from wood}) = \frac{10^{-3} \times 0.7}{1.5} = 0.5 \times 10^{-3}$$

$$\text{(b) } \phi\,(H_2 \text{ from wood}) = \frac{10^{-2} \times 0.2}{0.7} = 0.3 \times 10^{-2}$$

Because these quantum yield estimates were based on certain assumptions, only tentative conclusions can be made about their significance. If the values are approximately correct, it means that the efficiency of volatile product formation from wood in an inert atmosphere is somewhat lower than from cellulose. However, the order of magnitude is comparable.

If quantum yields are further estimated for volatile product formation from Douglas-fir during irradiation in air, higher figures are obtained: about 2×10^{-3} for $CO + CO_2$, and 0.7×10^{-2} for H_2. This would mean that wood is degraded in air somewhat more efficiently than cellulose, provided that the cellulose degradation is unaffected by the 2537 A wavelength in oxygen as has been reported (18).

Wood as a Variable

There is considerable variation in wood as a material. Differences in composition exist in various species. The ratios of the components (cellulose, lignin, extractives) may be different, and some components, such as extractives, differ chemically in various species of wood. There can also be variations within a tree: springwood and summerwood, heartwood and sapwood, compression wood and tension wood. Therefore, care is necessary when selecting samples for chemical experiments 1

A systematic study of wood as a variable was not done because it was considered more urgent to outline the degradation process in a general way and to develop satisfactory analytical procedures. Nevertheless, some examples of the effect of wood sample variation were obtained.

Springwood and summerwood.--Slices of springwood and summerwood were obtained from a fast-grown sample of southern pine (green) having wide springwood and summerwood bands, The slices were ground and equal weights (18 g.) of the two kinds of material were irradiated with the 2537 A light for a period of 168 hours in an air atmosphere. Gaseous degradation products were generated at different rates as shown in figure 21 and table 19.

Larger quantities of degradation products were obtained from springwood than from summerwood. Observations of wood weathering agree with this finding. Weathered wood shows considerably greater erosion of the springwood bands. However, some caution is needed in the interpretation of the results of irradiation experiments because of the difference in density between springwood and summerwood. Our measurements indicated that the specific gravity of springwood was 0.47 and 0.78 for summerwood. For equal weights of wood particles of the same size, the difference in specific gravity means that there was a larger surface area for the springwood particles. This could possibly result in an increased sate of degradation product formation from the springwood. On the other hand, differences in degradation rates for springwood and summerwood may arise because of differences in chemical composition. It has been stated (4, p. 73) that the lignin content is higher in springwood, and it is possible that lignin is degraded more rapidly. This question probably

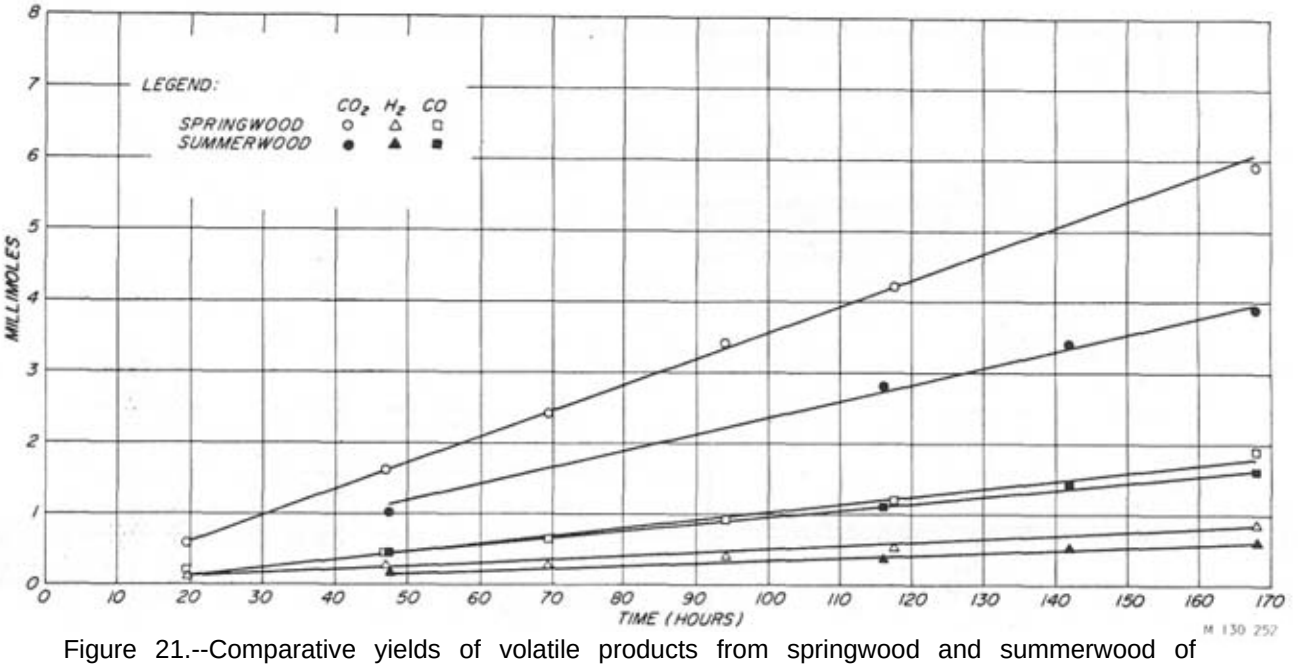


Figure 21.--Comparative yields of volatile products from springwood and summerwood of southern pine (ground wood) irradiated in air with a 2537 A light.

Table 19.--Volatile degradation products from southern pine ground wood irradiated in air with a 2537 A light

Material	Millimoles, total after 168 hours				pH before	pH after
	CO_2	CO	H_2	CH_3OH		
Springwood	5.9	1.9	0.85	0.24	4.17	3.40
Summerwood	3.9	1.6	.60	.30	4.23	3.48

could be resolved by irradiation of equal areas of springwood and summerwood in veneer form.

Effect of extractives.--It seemed likely that extractives in wood could influence the photodegradation process, serving either to accererate or retard the degradation. To estimate their role, extracted as well as unextracted Douglas-fir was irradiated. The ground wood was successively extracted with ethanol-benzene, ethanol, and hot water. The sample was irradiated with a 2537 A light source for 168 hours in the oscillating apparatus. The results are shown in table 20 and figure 22.

The extractives exerted a protective effect when irradiation was carried out in an air atmosphere, as smaller amounts of carbon dioxide and carbon monoxide were obtained from unextracted wood. The extractives could possibly be functioning as antioxidants. In an inert atmosphere the extractives appeared to have little significance.

Effect of species.--There is considerable variation in the chemical composition of various species of wood, The composition of extractives is often different and the ratios of wood components such as cellulose and lignin vary for different species. It is also known that differences exist between hardwood and softwood lignin. Therefore, differences in the photochemical degradation process can be expected for various wood species. veneers of Douglas-fir and yellow-poplar were irradiated with the 2537 A light in an air atmosphere. The quantities of degradation products that were collected in 168 hours are shown in table 21.

Table 20.--Volatile photodegradation products from extracted and unextracted Douglas-fir irradiated with a 2537 A light

Douglas-fir ground wood	Atmosphere	Millimoles, total after 168 hours			
		CO_2	CO	H_2	CH_3OH
Unextracted	Air	10.2	1.9	1.8	0.8
Extracted	....do....	14.1	5.6	1.5	.6
Unextracted	Nitrogen	.63	1.5	1.8	.16
Extracted	....do....	.8	.64	.5	.1

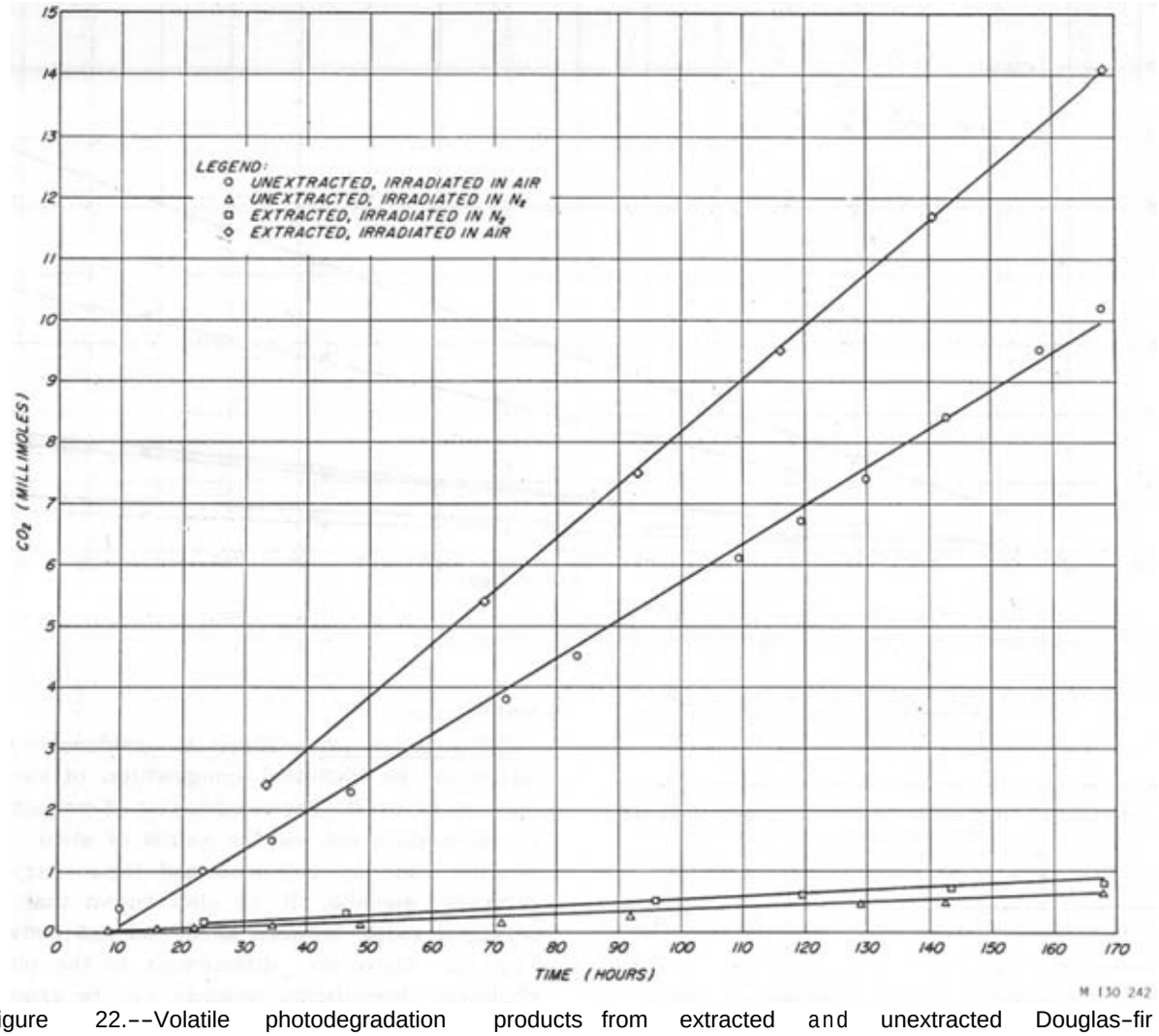


Figure 22.--Volatile photodegradation products from extracted and unextracted Douglas-fir irradiated with a 2537 A light.

Table 21.--Volatile degradation products from Douglas-fir and yellow-poplar veneers irradiated in air with a 2537 A light

Veneer species	Millimoles, total after 168 hours		
	CO_2	CO	H_2
Douglas-fir	6.12	3.41	1.68
Yellow poplar	9.46	5.72	1.00

The results showed that larger quantities of carbon dioxide and carbon monoxide were &-tained from yellow-poplar veneer.

In a similar fashion, veneers of redwood, yellow-poplar, and Douglas-fir were irradiated with a 3650 A light source in an air atmosphere for 168 hours. The quantities of volatile products are listed in table 22.

The results show that under these conditions of irradiation redwood was most susceptible to photodegradation, followed by yellow-poplar and Douglas-fir, in descending order. Experiments of this nature may be useful in evaluating species far their relative stability toward light.

Stabilization of Wood Against Degradation by Light

Ultraviolet light absorbers.--To protect materials such as plastics and coatings from harm-

Table 22.--Volatile photodegradation products from veneers of three species irradiated in air with a 3650 A light

Veneer species	Millimoles, total after 168 hours			
	CO_2	CO	H_2	CH_3OH
Douglas-fir	1.15	0.87	0.05	0.18
Yellow poplar	1.41	1.03	----	.09
Redwood	1.57	1.02	.25	.92

ful effects of light, ultraviolet light absorbers are often incorporated. The use of ultraviolet light absorbers to protect a wood surface has recently been disclosed in a patent (13).

It was of interest to estimate quantitatively the protective effect of an ultraviolet light absorber applied to a wood surface. The extent of degradation of the treated wood sample was determined by measuring the quantities of volatile degradation products that resulted from irradiation. This method was described earlier in the initial discussion of volatile products.

Dibenzoylresorcinol was applied to a Douglas-fir veneer from a saturated ethanol solution. The absorber was applied in two concentrations, 0.64 and 0.11 milligram per square centimeter. The treated veneer was irradiated with a 3650 A light source in an air atmosphere for 168 hours. Dibenzoylresorcinol absorbs strongly in this wavelength range. The comparison of the guantities of volatile products obtained in this and the control experiment showed that some protection for the wood was indeed provided. The quantity of carbon dioxide that was formed from the sample treated with the higher concentration of absorber was reduced by about 48 percent, and the quantity of the carbon monoxide was reduced by about 34 percent (table 23, figure 23). Somewhat less protection was provided by the 0.11 milligram concentration.

Table 23.--Effectof ultraviolet light absorber on the formation of volatile degradation products from Douglas-fir veneer irradiated with a 3650 A light

Treatment	Millimoles, total after 168 hours			
	CO_2	CO	H_2	CH_3OH
Untreated veneer	1.15	0.87	0.05	0.18
Dibenzoyl resorcinol treated (0.11 mg/cm^2)	.90	.64	.12	----
Dibenzoyl resorcinol treated (0.64 mg/cm^2)	.60	.58	.50	.02

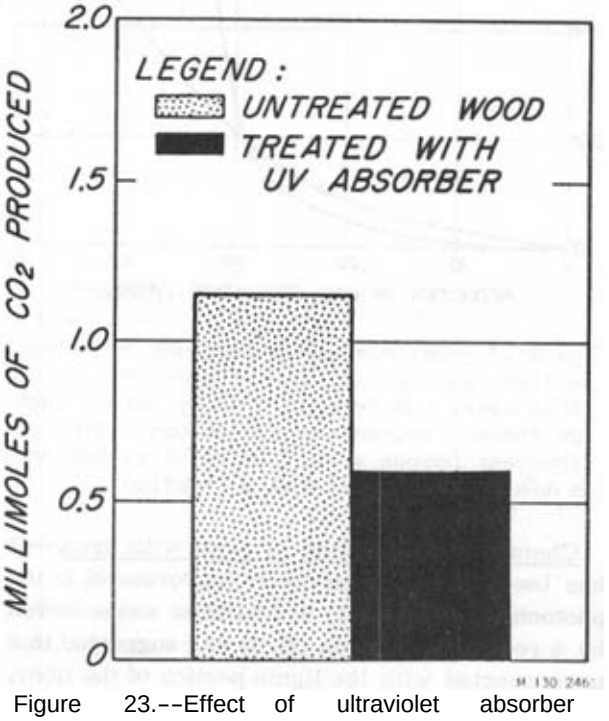


Figure 23.--Effect of ultraviolet absorber (dibenzoylresorcinol) on the photodegradation of wood.

By using this method of estimating photodegradation of wood, the optimum concentration of a chemical, such as an ultraviolet light absorber. on wood can be determined. When the concentration of the light absorber is plotted against the percent decrease in the degradation product formation, an estimate of the optimum concentration of the absorber can be made (figure 24).

Quantitative measurement of the degradation products is a relatively rapid means for evaluating protective measures for wood. The irradiation was continued for a week and only occasional attention was necessary. Refinement of techniques may shorten the time needed. By contrast, artificial or natural weathering tests need a relatively long exposure time, which unfortunately postpones the conclusions. In addition, quantitative gravimetric determinations may be more reliable than visual evaluation.

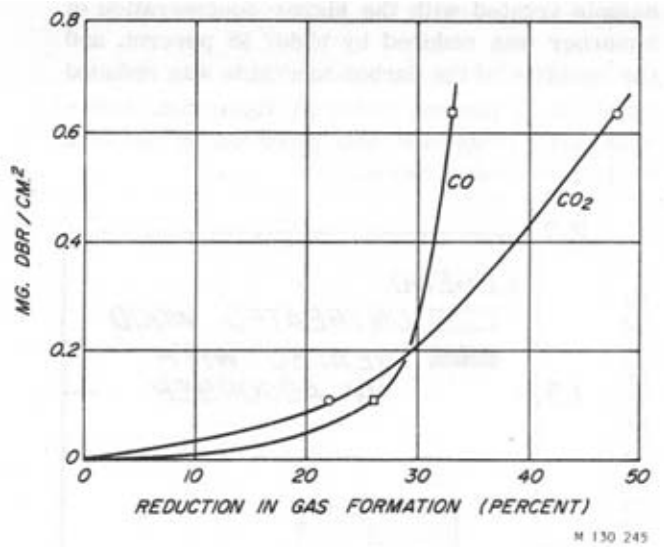


Figure 24.--Optimum concentrations of ultraviolet absorber (dibensoylresorcinol in this case) can be predicted by curves such as these. Increasing the concentration of absorber beyond a certain point yields only a minimum of additional protection.

Chemical modification of wood with urea--It has been reported that some improvement in the photochemical stability of jute fiber was achieved by a reaction with urea (2). It was suggested that urea reacted with the lignin portion of the fiber. Therefore, a similar effect could be expected in the case of wood.

Douglas-fir ground wood was heated for 2 hours in an aqueous solution of 50 percent urea and 1 percent cupric chloride catalyst in an oven maintained at 140° C. The wood was then washed repeatedly with boiling water, and dried. The treatment changed the color of wood to dark brown. Analysis indicated a nitrogen content of about 0.75 percent. Untreated softwood contains about 0.2 percent nitrogen (4, p. 74).

Urea-treated wood was irradiated for 168 hours with the 2537 A light in an air atmosphere. The formation of gaseous degradation products from urea-treated and untreated Douglas-fir during irradiation are shown in table 24 and in figure 25.

It appears that some protection from the effects of light was provided by the chemical modification of wood. This illustrate s one possible approach toward stabilizing wood against the damaging effects of light.

Table 24.--Volatile products from urea-treated Douglas-fir ground wood irradiated with a 2537 A light

Time	Millimoles, total after 168 hours		
	CO_2	H_2	CO
Hours			
0	----	----	----
22	1.24	0.15	0.19
46.5	2.16	.18	.27
120	4.91	.28	.96
144	5.82	.31	1.25
168	6.69	.34	1.52

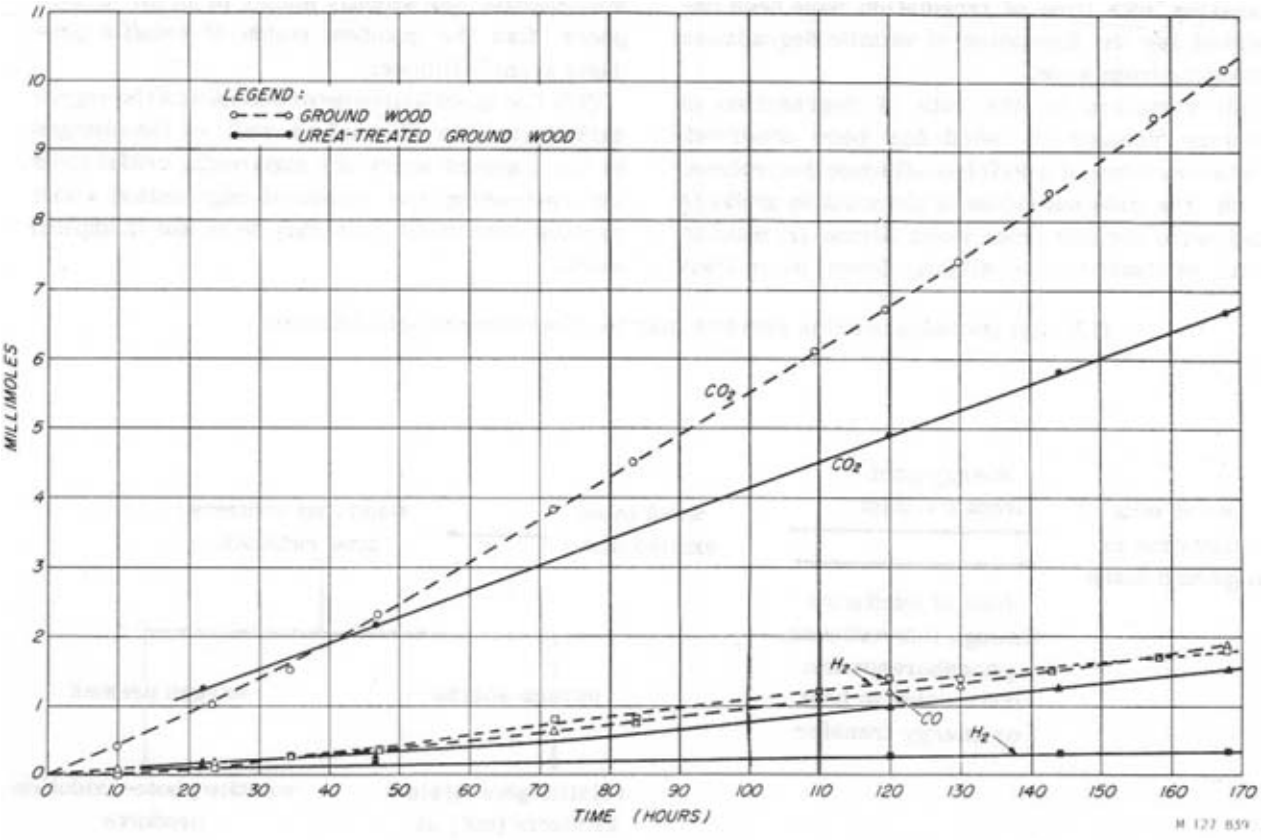


Figure 25.--The formation of volatile products from untreated and urea-treated Douglas-fir ground wood irradiated with a 2537 A light.

CONCLUSIONS

The results of this work and the previously published information have indicated some of the main features of the photodegradation process in wood. These can be summarized as follows:

(1) Wood is degraded by ultraviolet light. Some simple degradation products which have been identified are carbon monoxide, carbon dioxide, hydrogen, water, methanol, formaldehyde, organic acids, vanillin, and syringaldehyde.

(2) As a result of irradiation, the wood residue is chemically altered. The methoxyl and lignin content is reduced, the acidity and carbonyl concentration is increased, as is the ethanol solubility and especially the solubility in dilute base. Destruction of wood substance is visible on the surface under a microscope.

(3) Irradiation of wood produces free radicals in wood, even by the visible portion of light.

(4) In the presence of oxygen, photo-oxidation of wood is the dominant process in the middle as well as the near ultraviolet region.

(5) In an inert atmosphere or in vacuum, volatile products are also produced by middle ultraviolet but at a reduced rate. In the near ultraviolet range no volatile degradation products result.

(6) A post-irradiation effect exists in wood, as is shown by decreasing free radical concentration in the presence of oxygen and by the formation of volatile degradation products during storage in the presence of oxygen subsequent to irradiation in an inert atmosphere.

(7) Elevated temperature does not materially alter the rate of the degradation process. High humidity appears to accelerate degradation slightly. Constant rates as well as rates in-

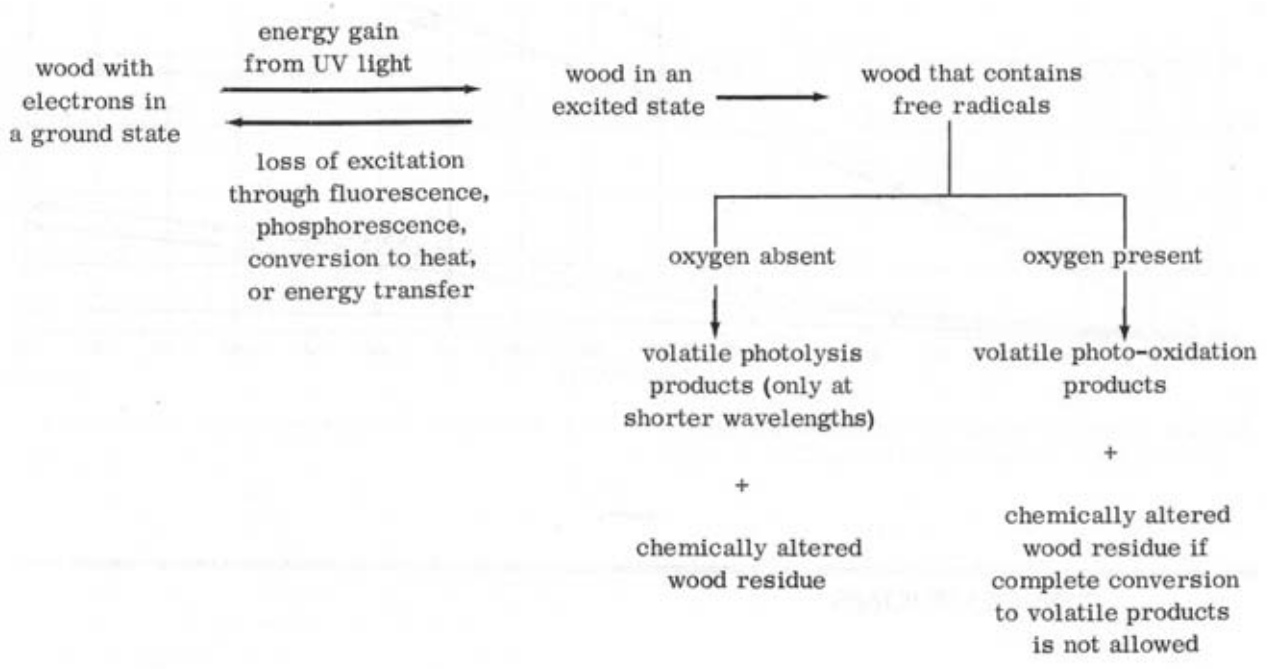
creasing with time of irradiation have been observed for the formation of volatile degradation products from wood.

(8) Variation in the rate of degradation of various species of wood has been observed. The extractives of wood also influence the process.

(9) The quantum yields of the volatile products that were formed from wood during irradiation were estimated to be slightly lower in an inert atmosphere, and slightly higher in an air atmosphere than the quantum yields of volatile products from cellulose,

(10) The quantitative determination of the degradation products of wood as well as the changes in the exposed wood are apparently useful tools for estimating the extent of degradation under various conditions, and may be of use in applied work.

(11) The photodegradation process may be illustrated by this scheme:



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