

Photochemical Degradation of Acetylated, Methylated, Phenylhydrazine-Modified, and ACC-Treated Wood*

M. A. KALNINS, *Forest Products Laboratory,† Madison, Wisconsin 53705*

Synopsis

If wood under clear, ultraviolet-transparent coatings could be protected from photodegradation, the performance of clear finishes would be greatly enhanced. The objective of this study was to determine whether acetylation or methylation of the wood and whether reaction with phenylhydrazine or treatment with acid copper chromate would impart resistance to photodegradation by longwave UV light. Infrared (IR) and ultraviolet (UV) spectra, analysis of wood before and after irradiation, and quantitative determination of volatile degradation products were used to measure degradation. Acetylation did not protect wood, although acetyl groups themselves were resistant to photodegradation. Methylation did not protect wood either, and methylated wood yielded more methanol and formaldehyde during photodegradation. Phenylhydrazine-modified wood lost the newly introduced nitrogen and failed to protect wood also. Acid copper chromate treatment allowed some demethoxylation, but severely curtailed the photooxidation process.

INTRODUCTION

Unfinished wood or wood that has been finished with clear coatings has won wide acceptance because of its attractive appearance. When it is exposed outdoors, however, the attractive appearance is soon lost.¹ In 2 years, the clear finish has often failed. Some clear films that are transparent to the ultraviolet (UV) portion of sunlight are by themselves durable. If a UV-transparent coating is used on wood, the wood under the coating is destroyed by a process of photooxidation,² and the clear coating, although intact, is left unsupported.³ Some clear coatings absorb UV light. These films are not durable themselves, although they tend to protect the wood beneath. Thus, another approach is indicated: if wood under the UV-transparent coating could be protected from degradation, the wood/coating combination should be durable.

The lignin portion of wood strongly absorbs UV light in contrast to the cellulose portion of wood.² Therefore, it could be anticipated that lignin would be the first point of attack in this destructive process. Callow⁴ studied the discoloration of jute in sunlight. He suggested that polyhydroxy structures were formed by demethoxylation of the lignin portion, and that a subsequent quinone formation resulted in the discoloration of jute. Acetylation greatly reduced the discoloration. He concluded that substitution of phenolic hydroxyls by acetylation

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† Maintained at Madison, WI, in cooperation with the University of Wisconsin.

prevented these reactions. Leary⁵ reported a similar finding. Methylation and acetylation of newsprint reduced the tendency of the material to undergo yellowing when exposed to carbon arc light. He attributed the yellowing to quinones or quinone methides, and pointed out that free hydroxyls are necessary for their formation. Adler's work on the oxidation of lignin model compounds (methoxyl-substituted phenols) has shown that methoxyl groups were eliminated in the form of methanol, and that *o*-quinones were formed if the phenolic hydroxyl group was unsubstituted.⁶

Therefore, it appeared likely that in the photooxidation of wood, one of the first steps is the oxidative demethoxylation of lignin, and that conversion of the hydroxyls into ester or ether groups would block these reactions.

Carbonyl compounds readily undergo photochemical reactions, frequently by elimination of carbon monoxide.⁷ It seemed probable that in wood where the carbonyl groups had been chemically transformed the reactivity in respect to light would be different.

The effect of chromates in reducing weathering and in improving the performance of finishes was described by Black,⁸ Black and Mraz,⁹ and Feist.¹⁰ More recently, Chang, Hon, and Feist¹¹ reported that treatment of wood surfaces with aqueous ferric chloride or chromic acid solutions resulted in protection from photodegradation. In that work a quartz, high-pressure, mercury vapor lamp was used, and degradation was observed with a scanning electron microscope. Pizzi¹² has reported the formation of complexes between chromic acid and guaiacol, and attributes the changes produced in wood surfaces to the formation of such complexes.

The objective of this study was to determine whether wood may be protected from photooxidation by acid copper chromate treatment or by chemical reactions which selectively react with carbonyl groups, or by reactions which add methoxyl and acetyl groups to the hydroxyls of wood components.

METHODS AND MATERIALS

Redwood and yellow-poplar vertical grain veneers, 0.25 and 0.2 mm thick, respectively, were used in this work. The veneers were cut with a veneer slicer, and samples of equal areas (184 cm²) were used.

Acetylation. Redwood veneer was acetylated by heating it in acetic anhydride to reflux with pyridine catalyst.

Methylation. Yellow-poplar veneer was methylated with a cold, concentrated NaOH solution and dimethyl sulfate as has been described.¹³

Reaction with Phenylhydrazine. Redwood veneer was submerged in ethanol, a few mL of acetic acid were added, and the mixture was heated to reflux. An excess of phenylhydrazine was added dropwise.

Acid Copper Chromate Treatment. The solution was prepared by mixing 6% copper sulfate, 9.2% sodium dichromate, 0.2% citric acid, and 84.8% water. Redwood veneer was then brushed with this solution so that the surface was thoroughly wetted. The veneer was then dried at room temperature.

Irradiation Apparatus and Analytical Procedures. The UV source was a "Rayonet" photochemical reactor (the Southern N. E. Ultraviolet Co., Middletown, Conn.). (The use of trade, firm, or corporation names in this publication is for the information and convenience of the reader. Such use does not constitute an official endorsement or approval by the U. S. Department of Ag-

riculture of any product or service to the exclusion of others that may be suitable.) The wavelengths of light ranged from about 300 to about 400 nm with peak intensity about halfway between. The veneer samples were placed in a quartz tube in the reactor and were irradiated for 1 week (168 h). A stream of dry air that was free of CO₂ was passed through the quartz tube, then through the cold trap and the tubes to absorb the gaseous decomposition products (mainly carbon monoxide and carbon dioxide), which were determined gravimetrically.

The veneers were analyzed for methoxyl, acetyl, Klason lignin, and nitrogen content by the customary procedures,¹⁴ using IR and UV spectra obtained with KBr pellets containing ground wood samples. Methanol and formaldehyde were condensed in a cold trap that was cooled with dry ice. Their concentration was determined by gas chromatography. More extensive details of experimental procedures have been described previously.²

Earlier research² indicates that photooxidation of wood is a continuing process whereby wood is progressively destroyed and converted into volatile products of degradation. The quantities of these products are a measure of the extent of degradation. In this study the volatile products of degradation were measured, as were the changes in the methoxyl, acetyl, nitrogen, and lignin content. This allows the author to follow the photooxidation process and evaluate effect of chemical modification on the stability of the wood.

RESULTS AND DISCUSSION

Irradiation of Redwood. The UV absorption spectra of unmodified redwood before and after irradiation showed definite differences in the region around 240 nm. Absorption in this region is characteristic of isolated lignin preparations.¹⁵ After irradiation, the absorption in that region was much less intense (Fig. 1); this reduction represents a change in the conjugated system.

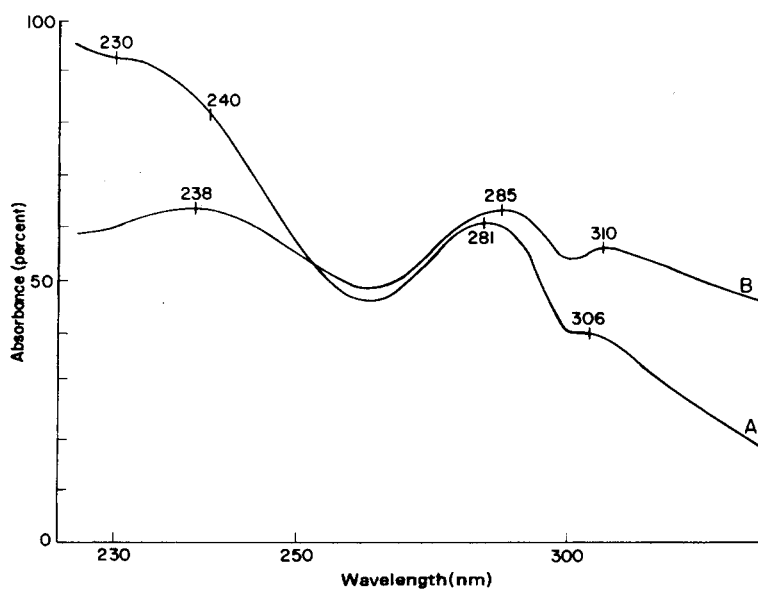


Fig. 1. UV spectra of (A) redwood veneer and (B) redwood after UV irradiation, showing changes in the conjugated system (ML83 5094).

The IR spectra of unmodified redwood before and after irradiation show differences at about $5.8 \mu\text{m}$, the absorption band being stronger after exposure. This is due to newly formed carbonyl groups.² The changes in methoxyl, lignin, and acetyl content of redwood resulting from irradiation are listed in Table I.

Irradiation of Acetylated Redwood. As a result of the acetylation reaction, the acetyl content of redwood veneer was increased from 1.70% to 24.98%. Acetylated and unmodified redwood samples were analyzed before and after exposure to UV light. The loss of methoxyl groups was greater from acetylated wood (Table I).

The acetyl content in the unmodified as well as the acetylated wood was not greatly reduced by irradiation. Evidently, the acetyl groups are not readily removed during photooxidation. Thus, acetyl groups in acetylated wood represent localized sites on a molecular level that are relatively stable in respect to light.

The IR spectra showed that the band at about $5.7 \mu\text{m}$ was stronger after acetylation (ester carbonyl). Irradiation did not significantly alter the IR spectrum of acetylated redwood.

The UV spectra of redwood and acetylated redwood showed only minor differences. Irradiation of acetylated redwood caused very slight changes in the UV spectra—the spectrum-producing chromophores must have remained essentially intact.

During irradiation, significantly larger quantities of carbon dioxide, carbon monoxide, methanol, and formaldehyde were formed from acetylated wood than from the unmodified wood (Table II). Thus, acetylation seems to magnify the adverse effects of UV light on wood. It is likely that the acetyl groups somehow facilitate the photooxidation process without themselves being destroyed.

Epoxides and isocyanates also react with the hydroxyl groups of wood to form ethers and urethane groups, respectively. Lack of protection from accelerated weathering of wood chemically modified with butylene oxide and methyl isocyanate was reported by Rowell, Feist, and Ellis^{16,17} based on weight loss and rate of erosion. Filling the lumens with methyl methacrylate and then polymerizing it improved stability by itself or in combination with chemical modification.^{16,17}

Irradiation of Yellow Poplar. As a result of the methylation reaction, the methoxyl content of the yellow-poplar veneer was increased from 7.3% to 22.1%. The methoxyl and lignin content of unmodified yellow poplar was reduced by UV light (Table I). IR spectra before and after irradiation show that a band at about $5.8 \mu\text{m}$ (carbonyl) was strengthened (Fig. 2) much the same as for redwood.

Irradiation of methylated yellow poplar produces a smaller decrease in the lignin content. The lignin content was reduced, however, during methylation. Evidently, other reactions in addition to methylation took place. The IR spectra show that methylation of yellow poplar reduced the hydroxyl band at about $2.9 \mu\text{m}$, and the carbonyl band at about $5.8 \mu\text{m}$ (Fig. 2). The reduction in the intensity of the hydroxyl band was undoubtedly due to the formation of methyl ether linkages. The other change is less obvious. Extraction of carbonyl-containing material or perhaps acetal formation may have been involved.

The UV spectra show that the absorption in the 240-nm region was reduced by methylation, presumably the effect of the introduced methoxyl groups. Ir-

TABLE I
Chemical Changes Caused by UV Irradiation of Unmodified and Modified Wood

Species treatment irradiation	Methoxyl (%)	Change (%)	Klason lignin (%)	Change (%)	Acetyl (%)	Change (%)	Nitrogen (%)	Change (%)
Redwood								
Unmodified								
Unirradiated	6.16		43.59 ^a		1.70		—	
Irradiated	5.65	-8.3	36.05 ^a	-17.3	1.67	-1.8	—	
Acetylated								
Unirradiated	4.97		28.08		24.98		—	
Irradiated	3.92	-20	23.21	-17.4	24.67	-1.2	—	
Modified with phenylhydrazine								
Unirradiated	4.94		37.32		—		4.63	
Irradiated	4.03	-18.5	33.82	-9.4	—		0.53	-88.5
Chromate-treated								
Unirradiated	6.61		34.28		—		—	
Irradiated	5.72	-13.5	33.83	-1.3	—		—	
Yellow poplar								
Unmodified								
Unirradiated	7.3		22.09		—		—	
Irradiated	6.22	-14.8	14.32	-35	—		—	
Methylated								
Unirradiated	22.1		17.59		—		—	
Irradiated	26.66	+20.7	15.57	-11.4	—		—	

^a Unextracted.

TABLE II
Products Resulting from UV Irradiation of Unmodified and Modified Wood

Species treatment	CO ₂ (mg)	Change (%)	CO (mg)	Change (%)	CH ₃ OH (mg)	Change (%)	CH ₂ O (mg)
Redwood							
Unmodified	42.2		14.8		0.7		Trace
Acetylated	55.1	+30	21.3	+44	2.9	+314	2.2
Phenylhydrazine-modified	42.9	+1.7	12.4	-16	1.5	+115	Not detected
Acid copper chromate-treated	8.4	-80	1	-93	trace		Not detected
Yellow poplar							
Unmodified	40.1		12.2		1.9		Trace
Methylated	50.5	+26	25.8	+112	14.5	+674	7

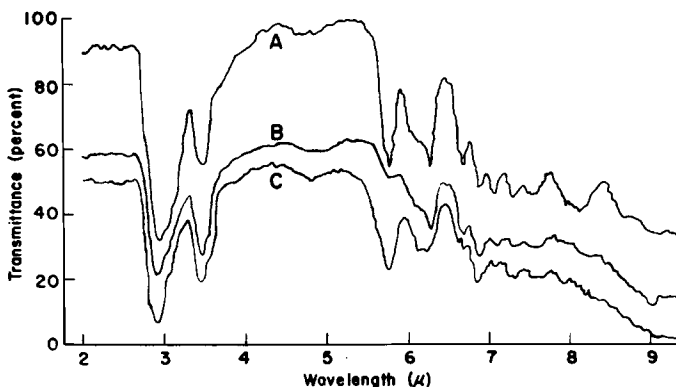


Fig. 2. Changes in absorption due to carbonyl groups in infrared spectra of (A) yellow poplar, (B) methylated yellow poplar, and (C) methylated yellow poplar after UV irradiation (ML83 5095).

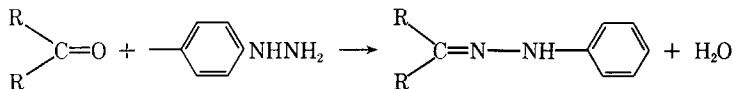
radiation of methylated as well as unmethylated yellow poplar produced only slight changes in the UV spectra.

After irradiation, methylated wood had a higher methoxyl content. This indicated that methoxyl groups were not easily removed during exposure to UV light. (This finding accounts for the insignificant changes in the UV spectra.) Some other portion of wood was lost at a faster rate, thus leaving a residue with a higher methoxyl content. The IR spectra indicated that irradiation of methylated wood strengthened the absorption at about $5.8 \mu\text{m}$ (carbonyl).

In comparison to unmodified wood, larger quantities of volatile products of degradation were obtained when methylated wood was irradiated (Table II). Percentagewise, the quantities of methanol and formaldehyde increased strikingly. This strongly suggests that these two compounds originated in the methoxyl groups, even though demethylation did not proceed readily, as is shown by the higher methoxyl percentage after irradiation. The formation of formaldehyde and methanol is not difficult to explain if the methoxyl groups were eliminated as methyl or methoxyl radicals. Either oxidation or disproportionation reactions could account for these products. It is also evident from the data that methylation did not provide overall protection from degradation; the products of degradation were more abundant when the modified veneer was irradiated.

Both in this case and with acetylated wood, the substitution of another functional group for a hydroxyl hydrogen resulted in no overall improvement in the stability of wood (improvement had been suggested by Leary⁵). It may be true that the oxidation of phenolic hydroxyls was prevented, and, indeed, the methoxyl and acetyl groups were relatively more stable than other portions of wood, but no overall protection was provided. Leary's suggestion that acetylated or methylated wood might extend the lifetime of clear finishes is not likely to be sustained. No evidence of quinone structures was seen in the UV spectra of irradiated wood. Such groups had been suggested as intermediates in wood oxidation.^{4,5} Quinones have an absorption band at about 360 nm, but the spectra of irradiated redwood and yellow-poplar did not show absorption in that range. It may, of course, be a question of concentration. The quinoid structures may be present but in quantities too low to appear in the spectra.

Irradiation of Wood Modified with Phenylhydrazine. Chemical modification of redwood veneer with phenylhydrazine resulted in an increased nitrogen content (from 1.04% to 4.63%). Modification of wood with phenylhydrazine evidently occurred largely at the carbonyl sites:



Carboxyl groups also are reactive, but unimportant because of their low abundance in wood. The changes in the UV spectra show that wood was modified. The absorption in the region around 230–240 nm, was reduced after modification with phenylhydrazine [Fig. 3(B)], presumably attributable to conjugated system affected by carbonyl groups. The IR spectra were very similar before and after modification; it should be noted, however, that the C=N— and C=O groups show absorption bands in the same region.¹⁸

Figure 3 and Table I show that methoxyl loss during irradiation was larger in the modified wood. This evidently is related to the more abundant formation of methanol. The opposite was the case in the lignin determination. Apparently the modification of wood made methoxyl loss easier, but also lessened the extent to which degraded lignin is dissolved during the Klason lignin determination.

Carbon dioxide formation from the modified wood quantitatively was about the same as from the unchanged wood (Table II). Carbon monoxide evolution was somewhat reduced. Irradiation of the phenylhydrazine-modified wood produced chemical changes that altered the UV absorption spectrum profoundly (Fig. 3). The absorption maximum was shifted from the 235- to the 290-nm range, and there was another maximum at about 316 nm [Fig. 3(C)]. As is seen in Table I, the nitrogen content was reduced greatly. It appears likely that with

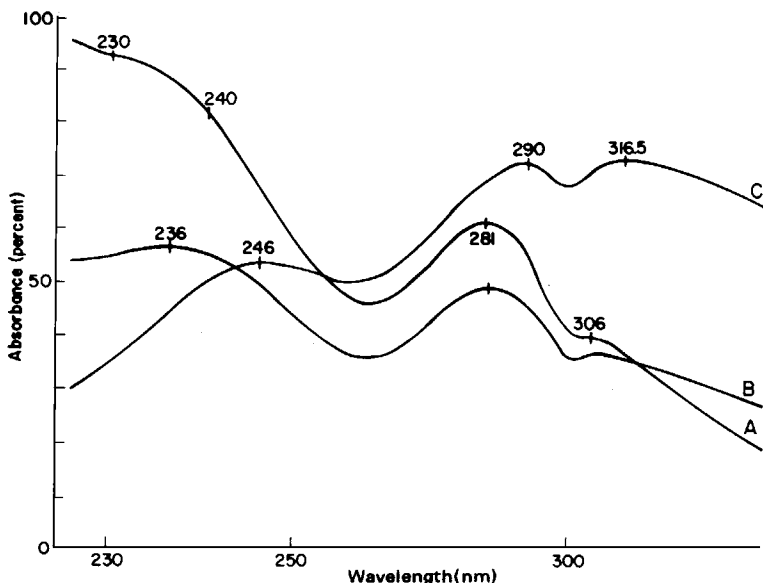


Fig. 3. UV spectra of (A) redwood, (B) redwood after reaction with phenylhydrazine, and (C) after reaction with phenylhydrazine and after UV irradiation, showing changes in absorption due to conjugated system (ML83 5096).

the elimination of nitrogen, a rearrangement of phenyl groups occurred, thereby causing the marked changes in the aromatic nucleus, resulting in a different ultraviolet absorption spectrum. The IR spectra show that the carbonyl band increased in intensity as a result of irradiation.

Irradiation of Wood Treated with Acid Copper Chromate Solution. The treatment of wood with the acid copper chromate solution caused only very slight changes of the UV and IR spectra. The wood was changed in color to a dark brown, but the analyses show that only the lignin content was decreased appreciably (Table I). It appeared that only minor chemical modification took place. Using electron spectroscopy for chemical analysis (ESCA), Williams and Feist¹⁹ recently showed evidence of oxidation by chromic acid treatment of lignin and possibly extractives in wood to acetals and ketones. When a UV spectrum of treated wood was obtained without a prior washing, the sample had absorption characteristics both of the chromate solution and of lignin. Therefore, it is clear that a portion of the light was absorbed by the copper chromate. Because wood is indeed protected by the treatment, some form of harmless dissipation of energy by the copper chromate must be occurring. The possibility of some kind of energy emission was suggested by Chang, Hon, and Feist¹¹ as one of the mechanisms whereby wood is protected from photodegradation by chromic acid. In a study of photoluminescence from wood, no emission from acid-copper-chromate-treated wood was detected in the visible range.²⁰

From Table I it is seen that a somewhat larger methoxyl loss was experienced by the treated wood. Lignin loss, however, was very slight. The formation of volatile degradation products was reduced radically as is shown in Table II.

Evidently, a definite protective effect is provided when wood is treated with the chromate solution, which functions at least as a UV light absorber and possibly by other mechanisms as well. After exposure of the treated wood to UV light, a slight increase in the band at about $5.8 \mu\text{m}$ (carbonyl) was noted in the IR spectrum.

After irradiation, the UV spectrum showed a reduced absorption in the region around 240 nm (Fig. 4). This change was very similar to the change resulting from irradiation of untreated redwood. In fact, the spectra are nearly identical (Fig. 4). Evidently, the alteration of the substituted conjugated carbonyl chromophore by irradiation was similar in both treated and untreated redwood. It is likely that the spectra reflect loss of methoxyls from an aromatic ring that was responsible for the original spectrum. The most striking effect of the chromate treatment appears to be in stopping photooxidation short of completion (simple volatile degradation products such as H_2 , CO , CO_2 , CH_3OH , etc., were not readily formed) possibly by a mechanism that involves complexing of hydroxyls as suggested by Pizzi¹² and Williams and Feist.¹⁹

CONCLUSIONS

UV irradiation of redwood produced major changes in the conjugated system. The changes included formation of additional carbonyl groups. Acetylated redwood, contrary to expectations, was not more resistant to photodegradation. Larger quantities of volatile degradation products resulted, and more methoxyl groups were lost. Acetyl groups themselves were resistant to photodegradation and seemingly made the rest of wood more susceptible to photodegradation.

Methylation of yellow poplar did not make it resistant to photodegradation.

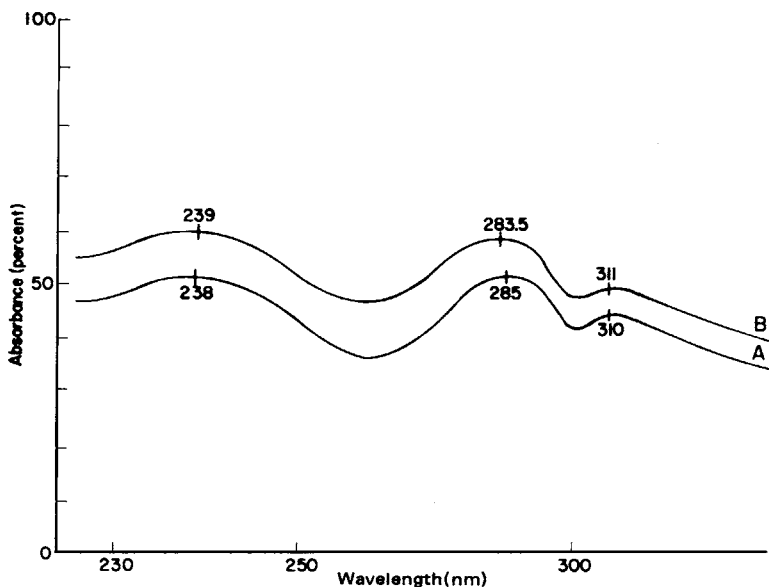


Fig. 4. UV spectra of (A) redwood after UV irradiation and (B) chromate-treated redwood after UV irradiation, showing similar changes in the conjugated carbonyl system (ML83 5097).

Larger quantities of volatile degradation products were formed, notably formaldehyde and methanol. The increased formation of methanol probably resulted from the introduced methyl groups. Demethylation during photodegradation was slower than other reactions (higher methoxyl content after irradiation).

Thus, substitution of hydroxyl groups in wood does not by itself prevent photooxidation reactions. Modification of carbonyl groups in wood with phenylhydrazine likewise did not protect wood from photodegradation, and the newly introduced nitrogen was readily eliminated.

Acid-copper chromate treatment caused some alteration of lignin. With the exception of a slightly increased methoxyl loss, photodegradation of the treated wood was greatly reduced. The exact mechanism of protection is not clear, but it is obvious that strong absorption of light in the UV range does occur. Irradiation produced similar changes in untreated redwood and in chromate-treated redwood in the conjugated system. Aromatic demethoxylation occurs in chromate-treated wood as it does in untreated wood, but the chromate treatment of wood prevents facile conversion of wood into volatile degradation products—the photooxidation process is stopped short of completion. The chromate treatment is not likely to be the best solution for the wood photodegradation problem because of the color change and the hazardous nature of chromium (VI) compounds. However, a clarification of the mechanism whereby wood is protected may suggest the use of more suitable substances.

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