

PHOTOPROTECTION OF WOOD SURFACES BY WOOD-ION COMPLEXES

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ABSTRACT

Mechanisms for protection of wood surfaces against weathering imparted by metal ions of inorganic salts, namely ferric ions and chromium ions, were elucidated. The lignin model compounds study revealed that the effectiveness of weathering protection is likely due to formation of complex between wood components and ferric chloride as well as chromium trioxide, which induced energy transfer to provide protection. The complex formation between lignin model compounds and metal ions was confirmed by the analyses of their infrared spectra, ultraviolet-visible spectra, and nuclear magnetic resonance spectra. These findings revealed that guaiacol and catechol reacted with metal ions to form water-insoluble complexes. Although cellobiose-ion complex was not isolated, it was evident by IR study that cellobiose participated in complex formation and accelerated the rate of complex formation. Like model compounds, it is plausible that wood-ion complexes being formed at the wood surfaces effectively blocked the free phenolic hydroxy groups, which are the reactive centers to initiate photochemical reactions, and thereby provided photoresistance to wood surfaces. It is likely that the complex systems are capable of minimizing photochemical reactions by energy transfer from wood to wood complexes, to emit effective energy harmlessly from wood surfaces. In addition, it is possible that wood-ion complexes might decompose peroxide impurities formed at wood surfaces to avoid photodegradation chain reactions.

Keywords: Weathering, ferric chloride, chromium trioxide, infrared and ultraviolet spectrophotometers, nuclear magnetic resonance.

INTRODUCTION

There is an increasing trend towards the use of wood for exterior applications. Unfortunately, the intricate outdoor environment is unfavorable to wood stability (Feist 1978a). It is known that unprotected wood surfaces are susceptible to weathering deterioration. Various deleterious environmental factors such as solar radiation, water, heat, and active atmospheric gases are involved in the deterioration reactions (Hon 1982). Because of the current shortage in supply and increased price of good-quality wood, many researchers have been making efforts to protect wood surfaces against weathering deterioration to prolong their service lives.

Many treatments have been reported to protect wood surfaces against weathering (Feist 1978a, b, 1979; Black and Marz 1974; Tarkow et al. 1966). One of the attractive approaches is to apply inorganic salts to wood surfaces. Several inorganic agents are currently proposed to treat wood surfaces as natural exterior finishes to improve the outdoor performance of wood. Of those available, salt systems based upon copper, chromium, and arsenic provide effective protection

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(Black and Marz 1974; Dolenko and Desai 1977). In addition, wood treated with chromium trioxide aqueous solutions exhibits improved dimensional stabilization, water repellency, and fungal resistance (Feist and Ellis 1978; Kubel and Pizzi 1981). Furthermore, Feist and other researchers (Feist 1978a, b, 1979; Chang et al. 1982) have recently reported that surface treatments with chromium compounds achieve protection of ultraviolet light-induced degradation. In addition to chromium trioxide, the degradative effect of ultraviolet light can also be reduced or prevented by treating wood surfaces with ferric chloride aqueous solution (Chang et al. 1982).

Although the effectiveness of ferric chloride and chromium trioxide treatments for increasing weathering resistance of wood has been demonstrated (Chang et al. 1982), the mechanisms responsible for such weathering protection are not yet completely understood. In order to increase the service life of polymers used outdoors, as a common practice, small quantities of ultraviolet stabilizers are added. These stabilizers are believed to impart photostability to polymers by absorbing deleterious ultraviolet radiation preferentially; by transferring of electronic energy from excited polymers; by scavenging free radicals; by preventing hydroperoxides formation; or by combination of these processes (Wiles and Carlsson 1981). Likewise, wood treated with ferric chloride and chromium trioxide exhibiting photostabilization effect should follow similar mechanisms. It is speculated that wood-ion complexes formed between wood components (i.e., cellulose and lignin) and inorganic ions may interfere with photochemical reactions by way of dissipating effective absorbed energy from the complexes to nondegradative form.

The objective of this study is to elucidate possible protection mechanisms for wood treated with ferric chloride and chromium trioxide. The roles of ferric chloride and chromium trioxide that lead to photostabilization and improved water repellency of treated wood are studied.

MATERIALS AND METHODS

Preparation of wood-ion complex compounds

Very diluted solutions of inorganic ions and lignin model compounds were prepared and stored at ambient temperature in order to control the reaction and obtain complex precipitates.

A designated amount of ferric chloride or chromium trioxide being dissolved in 200 ml of water was added to 50 ml of guaiacol or catechol aqueous solution with known concentrations. The solutions were then stored at ambient temperature for 48 h in which complexes were precipitated. The suspensions were centrifuged for 10 min, followed by decanting the liquid. The precipitates were washed in water and centrifuged again. This procedure was repeated three times. The precipitates obtained were first dried under vacuum at ambient temperature, followed by oven-drying at 105 C for 24 h.

Determination of formation of complexes

The precipitated complexes were analyzed by the following methods:

Infrared spectroscopic examination. The infrared spectroscopy used in this study was a model AccuLab-8 Beckman spectrophotometer equipped with a 100-line/

TABLE 1. *pH* values of solutions at different storage times during the preparation of complex compounds.

Complex	Storage time, day		
	0	1	2
Guaiacol-ferric chloride	2.8	3.1	3.2
Catechol-ferric chloride	2.8	3.1	3.2
Guaiacol-chromium trioxide	3.0	5.1	5.9
Catechol-chromium trioxide	5.1	6.0	6.1

mm grating to provide a spectral range of 4,000 to 600 cm^{-1} . A small amount of complex compounds was intimately mixed with pure, dry potassium bromide (KBr) powder. The resulting KBr disc was then immediately examined.

Ultraviolet-visible spectroscopic examination. For the determination of UV absorption, 0.2 mg of complex compounds formed was dissolved in 10 ml dioxane to give a 2% solution. The spectrum of this solution was recorded immediately or, in some cases, after a certain period of time, using a Cary-219 ultraviolet-visible spectrophotometer (Varian Assoc.).

Nuclear magnetic resonance spectroscopic examination. A certain amount of complex compounds formed was dissolved either in deuterchloroform or deuterodimethyl sulphoxide. The solution was examined by an EM-390 90 MHz nuclear magnetic resonance (NMR) spectrophotometer (Varian Assoc.). Tetramethylsilane (TMS) was used as an internal standard for all samples.

RESULTS AND DISCUSSION

Complexes formation

Chemical components of wood have a tendency to form complexes with inorganic ions. During pulping and papermaking processes, loss of brightness of paper can be attributable to the formation of colored complexes due to reactions between metal ions and lignin as well as phenolic compounds in wood fiber (Hart 1981). Likewise, we believe that ferric chloride and chromic acid are capable of forming highly colored complexes with catechol and guaiacol and, by analogy, with the guaiacol units of lignin.

During the preparation of complex compounds between ferric chloride and guaiacol (or catechol), the solution was initially clear and brown in color, which is the characteristic color of ferric chloride, but changed to orange (or blue-green) and finally purple (or blue-black) color with a dark purple (or black) complex precipitation. Likewise, when chromic acid was used, the solution was initially clear and yellow in color, but changed to purple (or brown-purple) color with purple (or black) complex precipitation. In addition to the color change, the change in pH of solutions was also noticed. The results, as shown in Table 1, revealed that the pH of the solutions increased during formation of complexes. This was ascribed to the consumption of part of inorganic ions when they were linked with guaiacol or catechol.

The complexes of guaiacol and catechol obtained were insoluble in water, when applied to wood surfaces; provide water repellency. The catechol-ion complexes

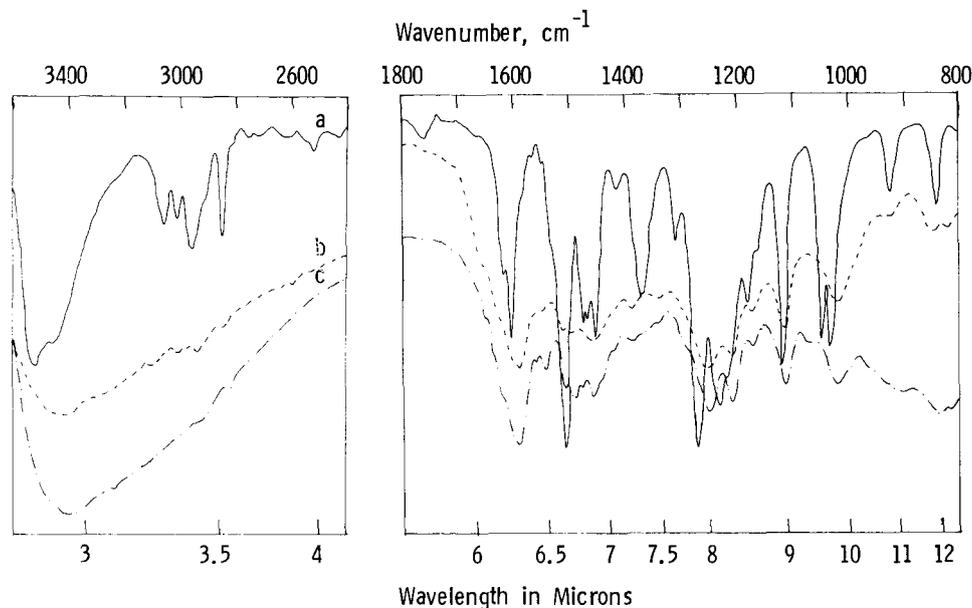


FIG. 1. Infrared spectra of a, pure guaiacol; b, guaiacol-ferric ion complex and c, guaiacol-chromic ion complex.

were insoluble in such organic solvents as benzene, toluene, carbon tetrachloride, acetone, methanol, ethanol, chloroform, and dioxane; whereas the guaiacol-ion complexes were insoluble in benzene, toluene, and carbon tetrachloride; and partially soluble in acetone, methanol, ethanol, chloroform, and dioxane. Nevertheless, none of the organic solvents could dissolve the complex compounds completely. This implied that metal ions were more strongly bound to the catechol than to the guaiacol. From the solubility characteristics, it appeared that two forms of complexes were presented: one possessing a stable chemical linkage between metal ions and catechol, which could not be dissolved by any organic solvents; the other seemed to be bound by an unstable linkage (or physical linkage), which was readily dissociated and resulted in partial dissolubility by some organic solvents.

Spectrophotometric examinations of precipitated complexes

The broadening of infrared bands of all the complexes was a good indication of the presence of chemical linkage and of the polymeric nature of the material. The infrared spectra of pure guaiacol, pure catechol, and their complexes with ferric ions and chromic ions are shown in Figs. 1 and 2, respectively. The absorption bands of pure guaiacol and catechol were sharp and strong, while the bands for complexes were broadened. An extremely broad -OH band at 3,500–2,400 cm^{-1} was observed from the complexes in comparison with pure guaiacol and catechol, indicating that -OH groups were probably bound with ferric and chromic ions.

When complex compounds were dissolved in organic solvents, the color of the solutions was purple, which would fade out after a period of time. By comparison

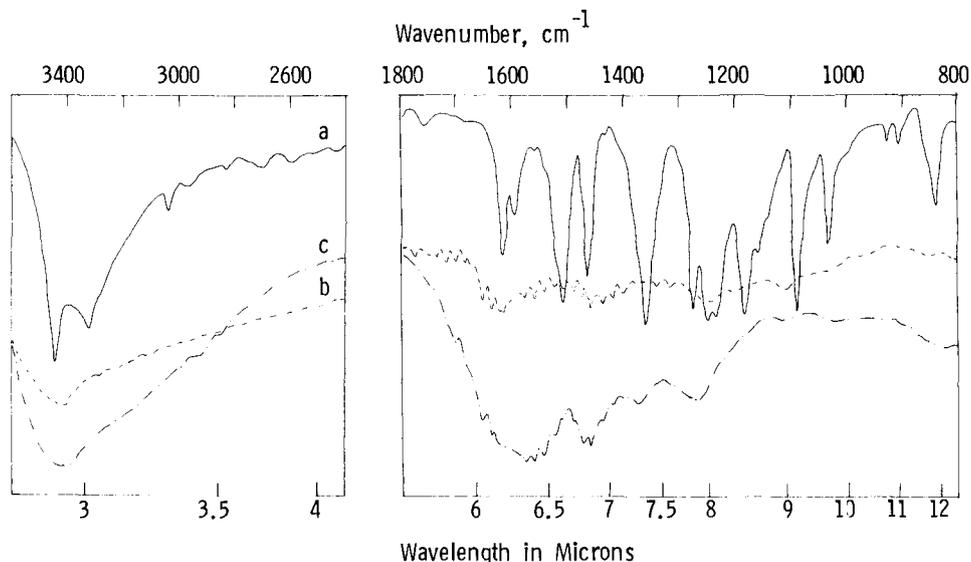


FIG. 2. Infrared spectra of a, pure catechol; b, catechol-ferrous ion complex and c, catechol-chromic ion complex.

with ultraviolet spectra (Fig. 3), the shift of an absorption band was recognized. The maximum absorption of pure guaiacol was located at 275 nm only, while two peaks were found at 262 nm and 480 nm for its complexes. After 2 h, 6 h, and 24 h of storage time, the changes of UV absorption were noticed. Thus, the absorption at 480 nm decreased, while the absorption band at 262 nm increased as a function of storage time. Again, this finding seemed to indicate that two forms of complexes were incorporated between metal ions and guaiacol.

The complex formation between guaiacol and ferric chloride and chromium trioxide was further substantiated by nuclear magnetic resonance (NMR) measurements. Part of the H-NMR spectra in deuterchloroform is shown in Fig. 4. The results of the H-NMR spectra indicated clearly that the signals of C_6H_4 and OCH_3 in complex compounds, as compared to the pure guaiacol, were markedly broadened and slightly downfield-shifted (to a larger δ). Furthermore, the signal of OH was not detected from complexes. It was possible that the signal of OH was shifted to a larger δ which could not be detected. Similar NMR spectra were obtained from complexes dissolved in deuterodimethyl sulphoxide.

For the purpose of clarifying if inorganic ions were attached to cellulose or to lignin, ferric chloride aqueous solution were added to cellobiose (as a model compound for cellulose) aqueous solution with and without guaiacol. No complex formation was found in cellobiose + $FeCl_3$ solution. However, the purple complex compound was precipitated from cellobiose + guaiacol + $FeCl_3$ solution, and there was noticeable difference in the rate of complex formation between cellobiose + guaiacol + $FeCl_3$ solution and guaiacol + $FeCl_3$ solution. The rate of complex formation was much faster in the presence of cellobiose. In addition, the infrared spectrum (Fig. 5) of a complex compound obtained from cellobiose + guaiacol + $FeCl_3$ solution demonstrated that cellobiose participated in the reac-

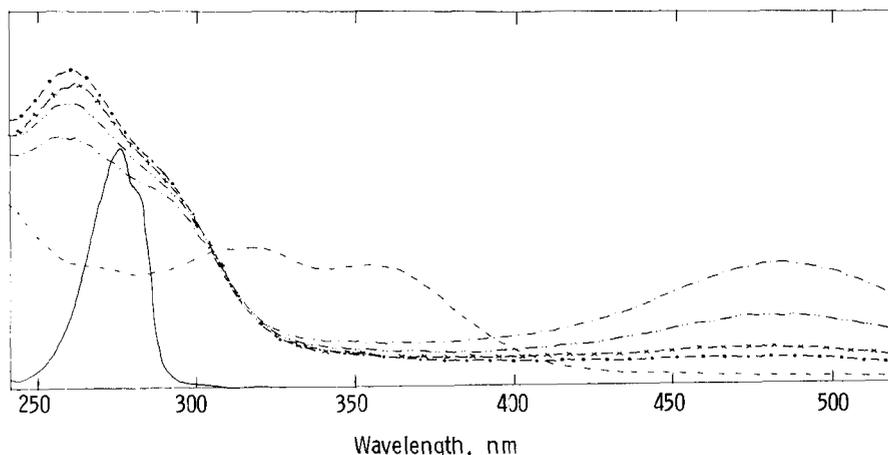


FIG. 3. UV absorption spectra of guaiacol (—), ferric chloride (---), and guaiacol-ferric ion complex, stored at 0 (···), 2 (-·-·-), 6 (-×-×-) and 24 h (-●-●-).

tion of complex formation, although complex compounds could not be precipitated out from cellobiose + FeCl_3 solution; the complex formation between carbohydrates and ferric ions could be detected by ultraviolet spectrophotometer (Hon 1975). A new absorption peak 360 nm due to complex formation was observed. Pizzi (1979) reported that glucose did not form insoluble complexes with chromic acid. It seemed to be possible that the complex compound might be formed between inorganic salts and cellobiose (or cellulose), but it was water-soluble so that complex compound could not be collected. Comparative experiments showed that no precipitation was obtained when ferric chloride was added to anisole or *O*-cresol aqueous solution. These findings suggested that adjacent -OH and -OR(H) groups were essential for the complex formation. Likewise, Tanaka and Senju (1965) found that the hydroxyl groups of liginosulfonate are functional to dichromate in the gelling reaction. The liginosulfonate-chromate and catechol-dichromate reactions were also studied by Hayashi and Goring (1965).

It has been shown that free phenolic hydroxyl groups are the reactive centers in the photodegradation of wood materials (Hon 1981; Kringstad 1969) to produce phenoxy radicals. From the standpoint of stabilization, the complex formation between phenolic OH and inorganic salts is certainly an advantage. It means that the blocking of free phenolic hydroxy groups would prevent the formation of phenoxy radical and thereby the photo-induced chain reactions cannot occur, or it is quite possible that the complex system may act as an energy transfer agent to deactivate the photoexcited chromophores in wood before they undergo chemical reactions that lead to photodegradation.

The formation of hydroperoxides produced in wood surfaces by light, as a result of interaction between free radicals with molecular oxygen, has been demonstrated earlier (Hon et al. 1982); and previous work by Polcin and Rapson (1972) has shown that heavy metal ions, particularly ferric ions, which form colored complexes with some wood components, have the ability to decompose a hydrogen peroxide bleaching agent. Accordingly, it is plausible that the formation of com-



FIG. 4. Part of the H-NMR spectra of a, pure guaiacol; b, guaiacol-ferric ion complex, and c, guaiacol-chromium ion complex, in deuteriochloroform.

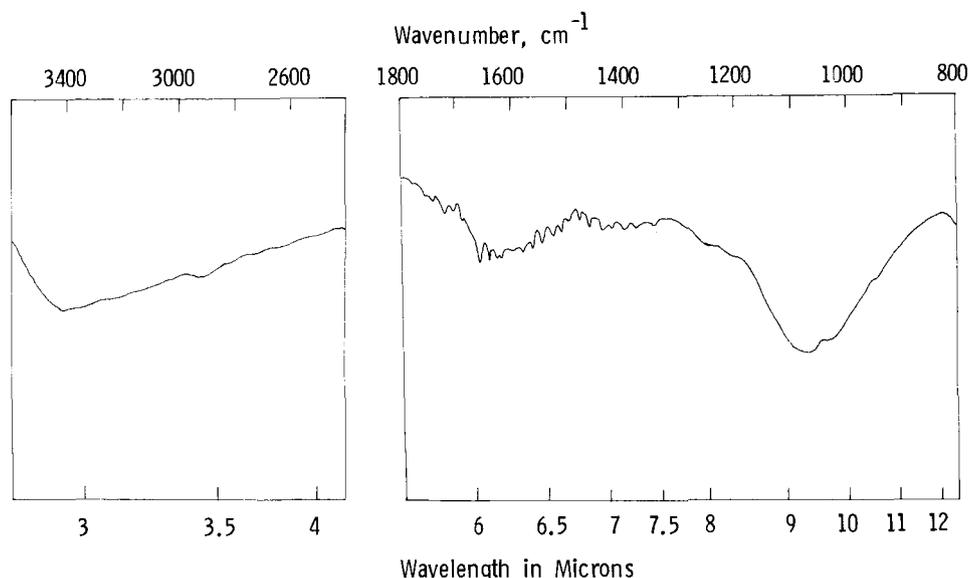


FIG. 5. Infrared spectrum of cellobiose-guaiacol-ferric chloride solution.

plexes between inorganic salts and wood components would decompose peroxides being formed at wood surfaces. The reduction of peroxide content would reduce the rate of photooxidation and prevent the formation of radical products from peroxide to initiate free radical chain reactions.

CONCLUSIONS

The formation of complexes between guaiacol and catechol and inorganic salts is confirmed by spectrophotometric analyses. It implies that wood components and inorganic salts are capable of forming similar complexes. The findings suggested that the blocking of free phenolic hydroxyl groups, which are reactive centers during photochemical reactions, provides photostability to wood surfaces. Although the exact action of the complexes is not clearly understood, it is likely that the newly formed complex systems between the inorganic ions, namely, ferric and chromium ions, and phenolic hydroxyl groups of wood components are capable of transferring or emitting effective energy from wood surfaces. The other possibility is that the presence of inorganic salts could prevent the formation of peroxides at wood surfaces and hereby reduce photodegradation.

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