THE INFLUENCE OF DIDECYLDIMETHYLAMMONIUM CHLORIDE (DDAC)
TREATMENT ON WOOD WEATHERING

by

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Vancouver, Canada

Date July 28, 1997
ABSTRACT

The potential of alkylammonium compound (AACs) as wood preservatives, was recognized during the 1970s. Two of the problems associated with AAC-treated wood, particularly treated with didecyldimethylammonium chloride (DDAC), are severe surface degradation and discoloration compared to ammoniacal copper quaternary ammonium compound (ACQ) and chromated copper arsenate (CCA) treated wood. The key objective of this study was to identify the mechanistic pathways by which DDAC affects wood weathering.

An FTIR technique was developed and employed to study the photodegradation of wood. The compositional changes in wood sections of various thickness following DDAC and ACQ treatment, and either natural weathering or UV irradiation were examined using FTIR spectroscopy. The studies on DDAC and ACQ fixation suggested that interaction between the preservative and lignin had taken place and that these preservatives favored fixation to lignin over cellulose. The natural weathering and artificial UV irradiation studies showed that DDAC accelerated wood weathering via enhancing wood photodegradation (mainly delignification), and that ACQ slowed wood photodegradation as demonstrated by inhibiting the formation of carbonyl groups and delignification.

The effect of DDAC, ACQ, and CCA treatments and their retention on wood photodegradation during weathering was investigated using FTIR and Ultraviolet-Visible reflectance spectroscopy. Delignification, demethoxylation, and cellulose degradation were accelerated by DDAC treatment, but slowed by both ACQ and CCA treatments. ACQ treatment also inhibited carbonyl formation. Those effects were enhanced by higher
preservative retentions. Weight loss of the weathered samples corroborated the FTIR and UV-Vis results. The comparison of the photodegradation of methylated and unmethylated wood demonstrated that both fixed and adsorbed DDAC must be involved in the photodegradation mechanism and that the fixation reaction of DDAC to lignin was one of the principal factors affecting wood photodegradation.

The studies using lignin model compounds in solution revealed that DDAC had no influence on the major photoreactions taking place in the solvent employed. The lack of significant DDAC-lignin interaction in solution most likely explains why the solution photochemistry failed to provide useful evidence of the pathway.

The ESR studies on the free radical formation and decay in wood revealed that DDAC functioned as photosensitizer. The fixed DDAC was essential for sensitization to occur while the adsorbed DDAC accelerated this process.
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<tr>
<td>AAC</td>
<td>Alkylammonium compound</td>
</tr>
<tr>
<td>ACA</td>
<td>Ammoniacal copper arsenate</td>
</tr>
<tr>
<td>ACQ</td>
<td>Ammoniacal copper quaternary ammonium compound</td>
</tr>
<tr>
<td>BMWM</td>
<td>Ball-milled wood meal</td>
</tr>
<tr>
<td>CC</td>
<td>Column chromatography</td>
</tr>
<tr>
<td>CCA</td>
<td>Chromated copper arsenate</td>
</tr>
<tr>
<td>DDAC</td>
<td>Didecyldimethyl ammonium chloride</td>
</tr>
<tr>
<td>DMA</td>
<td>Didecylmethylamine</td>
</tr>
<tr>
<td>DMBC</td>
<td>Dimethylbenzylcoco ammonium chloride</td>
</tr>
<tr>
<td>DRIFT</td>
<td>Diffuse reflectance fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>EPR</td>
<td>Electron paramagnetic resonance</td>
</tr>
<tr>
<td>ESCA</td>
<td>Electron scattering for chemical analysis</td>
</tr>
<tr>
<td>ESR</td>
<td>Electron spin resonance</td>
</tr>
<tr>
<td>EW</td>
<td>Earlywood</td>
</tr>
<tr>
<td>FeCl3</td>
<td>Ferric chloride</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
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<tr>
<td>FTIR-IRS</td>
<td>Internal reflectance fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatography</td>
</tr>
<tr>
<td>GC-MC</td>
<td>Gas chromatography mass spectroscopy</td>
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<tr>
<td>HPLC</td>
<td>High performance liquid chromatography</td>
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<tr>
<td>IR</td>
<td>Infrared spectroscopy</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>KBr</td>
<td>Potassium bromide</td>
</tr>
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<td>LMC</td>
<td>Lignin model compound</td>
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<td>LW</td>
<td>Latewood</td>
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<tr>
<td>MS</td>
<td>Mass spectroscopy</td>
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<tr>
<td>MIRIR</td>
<td>Multiple internal reflectance infrared spectroscopy</td>
</tr>
<tr>
<td>MWL</td>
<td>Milled wood lignin</td>
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<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
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<tr>
<td>PCP</td>
<td>Pentachlorophenol</td>
</tr>
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<td>PE</td>
<td>Polyethylene</td>
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<td>Polymer peroxy radicals</td>
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<td>Thin layer chromatography</td>
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<td>TMP</td>
<td>Thermalmechanical pulp</td>
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<td>Ultraviolet</td>
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<td>Ultraviolet-visible spectroscopy</td>
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To my parents

Mr. Changxun Liu and Mrs. Shuzhen Wang
Chapter 1

Background

Wood is a good light absorber due to the presence of several chromophoric groups (Hon and Glasser, 1979). When it is exposed to light of sufficiently low wavelength (UV light), photo-oxidation occurs and results in discoloration or yellowing, loss of gloss, roughening and checking (Chang et. al., 1982; Leary, 1967 and 1968). All of these phenomena reflect the chemical changes taking place during wood weathering.

It has been found that cellulose, hemicelluloses and lignin are all attacked by light during weathering. The breakdown of wood components by light is the first step of the deterioration of wood. Lignin is the major “culprit” in wood, interacting with light to initiate discoloration and deterioration. The interaction of wood and UV light is essentially a surface reaction in which free radical intermediates, generated by light, play a major role.

The methods adopted to prevent wood photodegradation include the use of inorganic treatments mainly with hexavalent chromium compounds (Feist, 1982 and 1983; and Feist and Hon, 1984), organic finishes, coatings or paints with UV absorbers and/or antioxidants, and chemical modifications. Preservatives can significantly influence wood weathering. With the growing application of treated wood products exposed without additional surface treatment and the development of new preservatives, the weathering aspects of treated wood have become of more importance. According to Feist and Hon (1984), the conventional preservatives, such as creosote, pentachlorophenol (PCP), and chromated copper arsenate (CCA), can improve surface
durability of wood with the trend of greater preservative content generally resulting in greater weathering resistance.

On average, treated wood is five times more durable than untreated wood (Hollick, 1993). Statistical data shows that in Canada, 70 million cubic feet of wood can be saved annually by using treated wood products (Hollick, 1993). In evaluating potential wood-preservative chemicals, four criteria should be addressed: safety, effectiveness, performance and economics. Conventional preservatives, such as PCP, ammoniacal copper arsenate (ACA) and CCA, are not environmentally friendly. Therefore, in the past two decades, a considerable amount of research activity has focused on the development of new wood preservative systems which generally exhibit lower mammalian toxicity without creating environmental hazards. Alkylammonium compounds (AACs) are one of these new candidates. AACs are colorless, possess low toxicity (used as household microbiocides, in shampoos and dish washing detergents), and most of them are soluble in both water and organic solvents. They possess a lower environmental impact than existing preservatives. The potential of AACs as wood preservatives, was recognized during 1970s (Anonymous, 1977; and Butcher and Drysdale, 1977). The research on AACs as wood protecting agents has been summarized by several authors (Butcher et. al., 1977a; Nicolas and Preston, 1980; and Preston et. al., 1987). AACs have a broad range efficacy against decay fungi and insects with a threshold retention of 4 - 6.4 kg/m$^3$. They perform best in above ground applications, although formulations with borate have been developed for sapstain and mold control. Performance in ground contact has been mediocre due mainly to the biodegradation of AACs (Doyle, 1995; Zheng and Ruddick, 1995; Burgel et. al., 1996a and 1996b) and other factors such as leachability, ionic
interactions, and type of AACSs. This fact spurred research on the modification of AACSs with ammoniacal cupric salts (Butcher et. al., 1977b) and leaded to the development of ammoniacal copper quaternary ammonium compound (ACQ) systems which provided efficacy against both biodegradation and weathering (Archer et. al., 1993; Jin et. al., 1991). DDAC is the preferred quaternary ammonium compound (QAC) and CuO:QAC ratios of 1:1 and 2:1 gave the best performance in field trials and laboratory studies (Ruddick, 1987; Jin and Archer, 1991; Jin et. al., 1991; Archer et. al., 1993).

The problems with AAC-treated wood in field tests are severe surface degradation and discoloration compared to CCA and ACA treatments (Ruddick, 1983; Jin et. al., 1991). According to Jin et. al., wood samples treated with alkylammonium compounds (AACs), particularly DDAC, showed considerable latewood defibration and severe earlywood erosion. ACQ and CCA treated samples are far less prone to surface weathering than either AAC-treated wood or untreated controls. FTIR spectral data of the surface material of specimens treated with DDAC and ACQ after exposure in the weatherometer, indicated that after 400 hr exposure DDAC-treated samples showed a significant loss of lignin. ACQ-treated samples did not show the same changes even after 1600 hr exposure. It was suggested that the enhanced photodegradation might be due to the AAC being fixed to lignin, which might promote delignification (Jin et. al., 1991). However, the mechanism by which these preservatives affect the weathering resistance of wood are still unclear.
The objectives of this study were

1. to examine the relationship between DDAC fixation and weathering;
2. to investigate the mechanistic pathways by which DDAC influence the photodegradation of wood; and
3. to determine how ammoniacal copper salt overcomes the influence of DDAC in the photodegradation of ACQ-treated wood.

The ultimate goal of this research is to understand the underlying chemistry of the weathering of AAC-treated wood. This knowledge will allow industry to develop treatments and processes that alter the characteristics associated with AAC treatments.
Chapter 2

Literature Review

2-1. Wood Composition

Wood is composed of cellulose (43-50%), hemicelluloses (28-38%), lignin (16-33%) and extractives (2-8%). As far as the chemical components of wood are concerned, a distinction must be made between the main macromolecular cell wall components cellulose, hemicelluloses and lignin. The proportions, chemical composition, and structure of lignin and hemicelluloses differ in softwood and hardwood, while cellulose is a relatively uniform component of all woods.

Cellulose is the major component of wood, making up approximately one half of both softwood and hardwood. Cellulose is characterized as a linear high-molecular-weight homopolymer built up exclusively of β-D-glucose. It has a strong tendency to form intra- and intermolecular hydrogen bonds. The glucose molecules in cellulose are present in the C-1 chair conformation with the three hydroxyl groups all equatorial. Native cellulose is partially crystalline (60-70% of wood cellulose) depending on the origin of the sample.

Lignin is the second most abundant renewable organic source after cellulose. It was named in 1865 by F. Schulze from the Latin word for wood (lignum). It is a three dimensional natural polymer composed of phenyl-propane units, linked together by various C-O-C and C-C bonds (Figure 2-1-1) (Goring, 1971; and Glasser et al, 1982).
Although many aspects of its chemistry still remain unresolved, lignin is characterized as having a complex structure, which absorbs ultraviolet (UV) light strongly, resulting in a relatively rapid discoloration (Gierer and Lin, 1972). This characteristic is of importance in both industrial applications and in the research of the structure and function of lignin in defining the properties of wood, such as wood weathering and preservative fixation.

Figure 2-1-1. Substructure (1)-(6): principal linkage mode between monomeric phenylpropane units in lignin polymer (softwood) (Sjöström, 1981).
There are three precursors of lignin: \( p \)-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Sarkanen and Hergert, 1971). The three monomeric precursors are present in variable proportions depending on several factors, one of which is the wood species. Softwood lignin contains predominantly coniferyl type structures, while lignin in hardwood is comprised of approximately equal amounts of coniferyl and sinapyl units with smaller quantities of \( p \)-coumaryl alcohol derived units. Each sub-unit of softwood lignin carries one phenolic oxygen and one methoxyl group, while in hardwood lignin approximately half of the units contain an additional methoxyl group. The functional groups of lignin are shown in Table 2-1-1. The lignin content of woody materials varies largely with wood species. Using the Klason method of extraction, normal softwood contains 26-32% lignin, while hardwood has 20-28% (Sjöstrom, 1981).

Table 2-1-1. Functional groups of lignin per 100 C\(_6\)C\(_3\) units (Alder, 1977)

<table>
<thead>
<tr>
<th>Group</th>
<th>Spruce lignin</th>
<th>Birch lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>methoxyl</td>
<td>92-96</td>
<td>139-158</td>
</tr>
<tr>
<td>phenolic hydroxyl</td>
<td>15-30</td>
<td>9-13</td>
</tr>
<tr>
<td>benzyl alcohol</td>
<td>15-20</td>
<td>N/A</td>
</tr>
<tr>
<td>noncyclic benzyl ether</td>
<td>7-9</td>
<td>N/A</td>
</tr>
<tr>
<td>carbonyl</td>
<td>20</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Polyoses (hemicelluloses) occur in close association with cellulose in the cell wall. These polymers are composed of five neutral sugars, the hexoses: glucose, mannose and galactose, and the pentoses: xylose and arabinose. Some polyoses contain additionally uronic acids. Compared to cellulose, the molecular chains in polyoses are much shorter, have side-groups and are branched in some cases. Their content in wood ranges from 18 to 35%. Hardwoods contain more polyoses than softwood and their sugar composition is different. Lignocellulosic complexes are hemicelluloses and lignin linked together by covalent bonds.

Cellulose and hemicelluloses are synthesized within the cell wall and deposited in the primary wall, forming a secondary wall during the phase of cell wall thickening. The formation of lignin begins before the cell wall thickening is complete, starting at the cell corners and spreading along the primary wall and intercellular layer. Cellulose as the skeletal substance, contributes its high tensile strength to the complex of wood structure. Hemicelluloses function as a temporary matrix before lignification. The role of lignin is to provide rigidity to the tree, making upright growth possible. Its concentration in the middle lamella cements individual cells together.
2-2. Wood Weathering

Wood is the most versatile and widely used structural material for indoor and outdoor applications. Because of its biological nature and sensitivity to light, unprotected wood is susceptible to weathering and photo-oxidative degradation. In 1827, Berzelius first reported the chemical phenomena of photo-oxidative degradation and discoloration. Since then, considerable research has been carried out on the photochemistry of wood degradation. Consequently, the key intermediates involved in the photodegradation of lignocellulosic materials and their degradation mechanisms are now understood reasonably well.

2-2-1. Phenomena of wood weathering

Weathering of wood, an undesirable surface phenomenon, refers to physical and chemical degradation at its surface and near-surface regions rather than biodegradation during exterior exposure. Wood weathering is predominantly a photodegradation process. It results from the combined actions of solar radiation, moisture, heat, wind and atmospheric factors (oxygen, air pollutants, etc.) (Feist and Hon, 1984; Hon, 1983; Hon and Chang, 1984). The first observable effect of weathering is usually a change in color, either a coloring of pale wood or a bleaching of colored wood. Microscopically, cell walls are destroyed and diagonal microchecks, expansion of apertures, and degeneration of pit domes are also observed (Hon, 1991a). The loss of gloss, roughening and checking can be observed on wood surfaces upon extended exposure. Figure 2-2-1 shows the
appearance of a softwood log after weathering for about 15 years (Feist and Hon, 1984). As weathering continues, rainwater washes out degraded portions and further erosion takes place.

Figure 2-2-1. Weathered surface of softwood after 15 years of exposure (in Madison, Wisconsin, USA) (Feist and Hon, 1984).
2-2-2. Major factors influencing wood photodegradation

The major factors affecting the natural photodegradation process of wood are chromophoric groups, incident radiation energy (wavelength), oxygen, moisture, impurities which act as sensitizers, temperature, and air pollutants.

The first law of photo-chemistry (the Grothus-Draper principle) states that, for a photochemical reaction to occur, some component of the system must first absorb light (Ranby and Rabek, 1975). The components of wood cellulose, hemicelluloses and lignin all satisfy the first law because of the presence of internal and external chromophoric groups (such as carbonyls, carboxyls, quinones, peroxides, hydroperoxides and conjugated double bonds, acetyl, etc.) (Gierer et al, 1973). External chromophoric groups are usually introduced by wood processing, heating, and exposure to light. Hon and Glasser (1979) classified the potential chromophoric groups in wood as follows:

**Chromophoric functional groups:** phenolic hydroxyl, double bonds, carbonyl groups etc.

**Chromophoric systems:** quinones, quinone methides, biphenyls etc.

**Leuco-chromophoric systems:** methylenequinones, phenanthrenequinones, phenyl-naphthalenediones, bimethylene-quinones etc.

**Intermediates:** free radicals.

**Complexes:** chelate structure with metal ions.
Figure 2-2-2. Ultraviolet spectra of (a) wood, (b) lignin, and (c) cellulose (Hon, 1991a).

Figure 2-2-3. Approximate bond energy of chemical bonds in wood (Hon, 1991a).
The UV absorption spectra of wood, cellulose and lignin (Figure 2-2-2) display their high absorptivity even in the sunlight wavelength range (> 290 nm). Light of sufficient energy to cleave chemical bonds is essential for photodegradation of wood to occur. Sunlight is capable of breaking down many chemical bonds present in wood (Figure 2-2-3) and induces the formation of wood polymer radicals. For example, carbon-carbon, carbon-oxygen and carbon-hydrogen bonds that form the basic backbone skeleton of wood components can be degraded with light of quantum energy at or above the value associated with their bond strength. Consequently, it causes a wide variety of chemical changes at the wood surface. Light-induced degradation of wood is strictly a surface phenomenon. UV light cannot penetrate deeper than 75 μm, and visible light no deeper than 200 μm into wood surfaces (Browne and Simonsen, 1957).

Beside the chromophoric groups and light, water and oxygen are also considered to be critical elements in wood photodegradation. Water molecules penetrate and swell the cell wall, leading to a reduction in hydrogen bonding. Due to their high polarity, water molecules may attract and interact with free radicals. It has been reported that moisture has a significant bearing on the formation and decay of free radicals in cellulose and wood exposed to UV radiation. Moisture content of cellulose in the range of 5-7% lead to a significant inhibition of free radical formation, but when the moisture content is lower or higher than this critical range, water appears to promote free radical formation (Hon and Feist, 1981, Hon et al, 1980). The free radical intensity of wood first increases as the moisture content in wood increases from 0 to 6.3% with a peak at 6.3%. The free radical intensity decreases with a moisture content higher than 6.3%. At 31.4% moisture content, the ESR signal was very weak (Hon, 1991a). The principal role of water molecules may
be that of facilitating light penetration into the accessible regions as well as opening up the less accessible regions for light penetration. It results in an incremental increase in the rate of free radical formation. The excess water molecules present probably trap free radicals to form a wood free-radical/water complex as shown in the following equation:

\[ \text{R-O}^- + \text{H}_2\text{O} \rightarrow [\text{R-O} \cdot \text{H}_2\text{O}]^- \]

where \( \text{R-O}^- \) represents a phenoxy radical.

Oxygen plays the role of an oxidant in wood photodegradation. Oxygen molecules react with free radicals resulting in the formation of polymeric peroxy radicals (POO-) and peroxides. Hon (1982) also suggested that the active free radical intermediates produced in cellulose, were immediately intercepted and stabilized by oxygen, prior to their combination and disproportion which occurred under vacuum. Larger amounts of free radicals were generated on wood surface under vacuum than in the air, for all light sources. This revealed that the interaction of radicals with oxygen probably leads to terminal reactions for some of the unstable free radicals, resulting in the formation of peroxides. According to Hon (1981a), oxygen is considered to be essential to activate the wood surface, by promoting free radical formation and hence photo-induced-oxidation of wood.

The other factors which should be considered include impurities, temperature, and air pollutants etc. Impurities, such as organic and inorganic sensitizers and oxidation products, may be introduced into wood during its mechanical and chemical processing.
They can stimulate the generation of free radicals by light. They can also widen the light absorption range of wood or create new absorption centers (Hon et al., 1982). The effect of light on the absorbance of wood and the intensity of free radicals increases in wood containing impurities. Heat may not be as critical a factor, as UV light and water, but as temperature increases, the rate of photochemical oxidative reactions increases (Feist and Hon, 1984). Freezing and thawing of absorbed water can also contribute to wood checking. Abrasion or mechanical action caused by such elements as wind, sand, and dirt can significantly affect the rate of surface degradation and removal of wood. Air pollutants (acid rain) are also factors that should not be neglected (Hon, 1994; Hon and Feist, 1993; Hon and Chao, 1988; Williams, 1987; and Raczkowski, 1980). Raczkowski (1980) reported that in the summer, the decisive factor in wood weathering is the intensity of solar radiation, whereas in the winter it is the increased amount of sulfur dioxide in the surrounding air (central European exposure). Williams (1987) found that the erosion of weathered wood increased following treatment by an acidic aqueous solution.

2-2-3. Physical and microscopic changes

Weathering of wood results in surface discoloration and leads to formation of macroscopic-to microscopic intercellular and intracellular cracks and checking. The bonding of cell walls near the wood surface loses its strength, resulting in defibration.

The first sign of changes at wood surfaces upon exposure to daylight, weathering or UV irradiation is yellowing. According to Hon (1981b), the changes in wood color follow a pattern of yellowing to bleaching, and eventually to brown, depending on the
exposure span. Leary (1967) reported that after exposure to UV irradiation, wood turned yellow, followed by bleaching. A similar color pattern was observed in lignin-rich pulps (Kringstad, 1969). The major cause of the color changes is due to the chemical conversion and degradation of lignin and extractives which readily interact with sunlight or artificial UV light (Hon, 1981b; and Feist and Hon, 1984).

The first sign of deterioration was an enlargement of the bordered pits apertures in radial walls of earlywood tracheids (Feist, 1984). Next, microchecks occurred. During weathering, the leaching and plasticizing effect of water apparently facilitate enlargement of the microchecks. Using SEM, Hon and Feist (1986) investigated the effect of weathering and artificial UV radiation on the micro structure of wood surface. The observed changes included loss of the middle lamella, separation of procumbent cells, and damage to the pit structure. The ultra structural studies of the Radiata pine (Pinus radiata) surfaces during weathering recorded erosion of the middle lamella after 30 days exposure and extensive separation of individual fibers at the interface of the middle lamella and secondary wall after 40 days of exposure (Evans and Thein, 1987). The gross physical changes of wood result from microscopic changes during weathering (Bamber and Summerville, 1980; Miniuttii, 1967 and 1970; and Borgin, 1970).

Erosion and checking differ in intensity because of different types of wood tissue on the surface, and the wood surface becomes increasingly uneven (Figure 2-2-1). Thus, the physical changes that occur in weathering can have a pronounced effect on the appearance of wood. Feist and Mraz (1978) reported an erosion value of 13 mm per century for western red cedar, and 6 mm per century for Douglas fir, the difference being related to their different densities.
The tensile strength of radial section sapwood strips 150 μm thick decreased to about 25% for Scots pine (*Pinus sylvestris*) and 5-10% for lime, during six months full weathering exposure in the summer at Prince Risborough (Derbyshire and Miller, 1981). However, this effect is only limited to wood surface (Feist, 1982 and 1983). The loss of strength is associated with a light induced depolymerization of lignin and cell wall constituents, and to the subsequent breakdown of the wood microstructure (Derbyshire and Miller, 1981).

2-2-4. Chemical changes

From the microscopic observations (Gellerstedt and Pettersson, 1975), the surface of weathered wood is seen to be rough due to the photodegradation of wood components and leaching of the photoproducts. All wood components can be attacked by UV light. According to Norrstrom (1969), lignin contributes 80-90%, carbohydrates 5-20%, and extractives about 2%, to the wood absorption coefficient of UV light, due to the differences in chemical structures, particularly in chromophoric functional groups. Chemical changes of wood photodegradation are mainly attributed to the light photosensitivity and the strong capability of autoxidation of lignin.

Forman (1940) in an early study concentrated on the chemical changes in lignin and the lignin component of wood meal caused by UV irradiation. After 170 hours in a weatherometer, the lignin content decreased from 27.5% to 18.0%, as determined by digestion with 72% sulfuric acid (Klason lignin method). Also, the methoxyl content
decreased from 4.97 to 3.04%. When lignin-containing materials (especially, wood and high yield pulp) were exposed to daylight, yellowing or discoloration became observable after a short period of the exposure (Kringstad, 1969; Leary, 1967 and 1968). This change is mainly due to the decomposition of lignin caused by light of wavelengths shorter than 350 nm. Significant color buildup or formation of chromophoric groups was recognized. Lignin absorbs UV light to produce chromophoric groups, such as α-carbonyl, biphenyl and ring-conjugated double-bond compounds, which respond to the ultraviolet irradiation and yield colored compounds. Lignin is not degraded by light longer than 350 nm, but photo-bleaching or whitening of lignin can be observed when it is exposed to light of wavelength longer than 400 nm. Severe losses in methoxyl content of wood materials on irradiation have been reported by several authors (Forman, 1940; Leary, 1968; and Kalnins, 1966). The chemical changes of lignin that have been identified include the reduction of methoxyl content and fragmentation of monomeric units (Leary, 1967 and 1968; Sanderman and Schlumbom, 1962; Kleinert, 1970; and Hon, 1988). Evans et al (1992a) have reported that the acid insoluble lignin content of Radiata pine veneers (85 μm in thickness) initially decreased rapidly over the first five days of natural exposure from 26.2% to 20.3%, and then continued to decrease at a lower rate with further exposure. The photo-oxidation and delignification of wood can be observed clearly from its UV-Vis and infrared spectra. The major peaks in the infrared spectra of plant polymers have been comprehensively assigned during the 1950s and 1960s (Hergert, 1971 and Marchessault, 1962). The chemical changes occurring in the wood components can be directly observed from the FTIR spectra of photo-exposed wood (Hon, 1983 and 1986; Hon and Chang, 1984; Hon and Feist, 1986; Hon and Chao, 1988; and Evans et al, 1992a
and 92 b) and pulps (Kimura et al, 1994 and Mitchell et al, 1989). The striking changes in the FTIR spectra of photo-exposed wood occur mainly at absorption bands 1720-1740, 1510 and 1265 cm⁻¹, which are related to wood photo-oxidation and delignification. Changes in photo-exposed pulps and lignin have also been examined using nuclear magnetic resonance spectroscopy (NMR) (Kimura et al, 1992 and Sjoholm et al, 1992). The photo-oxidation of wood has also been demonstrated by ESCA studies that show a higher oxygen content in photo-exposed wood surfaces than control (Hon and Feist, 1986). With UV-Vis spectroscopy the focus has been mainly on examining the nature of degraded products (Hon and Chang, 1984; Hon and Chao, 1988; Heitner, 1993; Castllan et al, 1993; Forsskahl and Tylli, 1993) and color reversion in the visible region (Hon and Chao, 1988; Forsskahl and Maunier, 1993; and Ek et al, 1993).

The increase in carbohydrate content of the weathered wood surface has also been reported (Kalnins, 1966). Although carbohydrates are much more stable to light than lignin, chemical changes can also take place in the polysaccharide portion of wood. Mass spectroscopic analysis substantiated that hydrogen, carbon monoxide, carbon dioxide and water were produced from cellulose irradiated with UV light (Hon, 1975). A series of mono- and oligomeric carbohydrates, such as xylose, D-glucose, D-arabinose, etc, were identified as degradation products from wood holocellulose (Kringstad, 1969).
2-2-5. Chemistry of wood photodegradation

*Studies on free radicals in wood*

Most of the photo-induced chemical reactions at the wood surface involve free radical formation (Hon, 1980). The immediate consequence of the interaction of wood with light is the generation of free radicals at the exposed surface. This has been proved by ESR spectrometry (Kalnins, 1966; Hon et al, 1979; Hon, et al, 1980, Hon, 1981a; and Hon and Feist, 1981). Hon, et al have extensively employed ESR to study the degradation of cellulose, lignin, and wood by UV irradiation (Hon, 1980; Hon, et al, 1980; Hon, 1989; Kringstad and Lin, 1970; Ogiwara and Kubota, 1973). These studies provided useful information on the intermediates of wood photodegradation during UV irradiation and weathering.

The formation, lifetime and reaction of free radicals are greatly dependent on the light sources, the exposure atmosphere and sample preparation and conditions. Normally, wood and wood fiber components contain small amounts of stable free radicals caused mainly by mechanical forces and exposure to light. Those radicals are detectable by ESR spectroscopy (Hon, et al, 1980; Ludwig, et al, 1971; and Steelink, 1972). Various studies have shown that green (freshly cut) wood and wood stored in the dark, contain no (or relatively few) free radicals (Hon, et al, 1980). The free radical content in fresh wood samples exposed to sunlight increases dramatically, but most of these free radicals are relatively unstable. Most of the free radicals are generated in wood during mechanical preparation as well as in wood exposed to electromagnetic irradiation. Exposure to artificial fluorescent light produces relatively few free radicals which are relatively stable.
at ambient temperatures. A much higher amount of free radicals are generated at wood surfaces exposed to UV light. Air-dried wood specimens readily interacted with a wide range of ultraviolet irradiation either in the presence of air or under vacuum to produce free radicals. The addition of oxygen to samples treated under vacuum tends to promote the formation of free radicals with relatively short life times (Chang, et al, 1980).

Although it is extremely difficult to identify free radical sites in macromolecular wood components, especially lignin, ESR studies have revealed some of the characteristics of free radicals during wood photo-irradiation. The formation of radicals from polysaccharides is greatly influenced by the presence of lignin (Feist and Hon, 1984), which tends to protect cellulose, so that radicals are produced predominantly from lignin molecules. In pure cellulose, free radicals are only formed in air when irradiated with wavelengths shorter than 340 nm. The studies of radical formation in various woods revealed that more free radicals are formed in earlywood than latewood, presumably due to the higher lignin content in the former (Hon and Feist, 1981). It's known that certain phenoxy radicals from lignin, and alkoxy radicals from cellulose, which make up the major portion of the singlet in the ESR spectrum of southern yellow pine after UV irradiation at -196°C, as well as carbon radicals generated from both cellulose and lignin, which make up the side-peak signals, decay rapidly (Hon, 1980). The chemistry behind the free radical formation and decay, has been proposed by Hon (1980 and, 1991a). The peroxo radicals generated on an irradiated wood surface seek to complete their unsaturated valences by a radical abstracting a proton from a nearby molecule to form a hydroperoxide. The hydroperoxide is relatively unstable toward heat and light, and is
usually transformed into a new chromophoric group such as a carbonyl or carboxylic group. The consequence of the free radical initiation, the free radical chain reactions or stabilization normally lead to discoloration, generation of new functional groups and degradation of the materials.

**Reaction Mechanisms**

The photolysis of lignin is initiated by the absorption of radiation energy. There are three important elements: the reactive groups available in lignin; the number of aromatic and phenolic sites and activated locations capable of interacting with light to initiate the discoloration and deterioration reactions; and energy-transfer effects leading to localization of the energy within the molecules resulting in splitting reactions such as depolymerization and dehydrogenation.

Because of the complexity of the structure of lignin, it is extremely difficult to identify the sites where free radicals are formed, as well as study the mechanisms of photodegradation of the natural lignin macromolecule. Thus, most studies of lignin photochemistry have been done by means of model compounds. Through the careful selection of model compounds, several important mechanisms of lignin photo-reactions have been identified.

*Hydrogen abstraction mechanism* Luners (1960) first proposed the photo-induced oxidation mechanism for the fragmentation of lignin and formation of colored quinone derivatives by light. Leary (1968) suggested that the free phenolic hydroxyl groups can be
considered to be the reactive centers in the degradation of lignified materials, as shown in Figure 2-2-4. According to his suggestion, units with such groups are first converted to phenoxy radicals, then demethylated and oxidized to colored quinoid degradation products. This suggestion was supported by the observation that blocking of the phenolic hydroxyl group by acetylation, benzylation or methylation could retard the yellowing of lignified materials.

\[
A \xrightarrow{hv, 355-440 \text{ nm}} A^* \xrightarrow{\text{AH}} \text{Yellow and demethoxylation products}
\]

where A represents a chromophoric group.

Figure 2-2-4: Hydrogen abstraction reaction
Subsequent studies have reported that carbonyl, biphenyl and phenolic groups, and ring-conjugated double bond structures appear to be mainly responsible for the photo-yellowing process (Lin and Kringstad, 1970a and b; Kringstad and Lin, 1970; Gierer and Lin, 1972; Brunow and Sivonen, 1975; Forsskahl, et al, 1981; Forsskahl, 1984; and Forsskahl and Tylli, 1984). Of these, the carbonyl chromophore is the most effective sensitizer. Both free phenolic hydroxyl and carbonyl groups are considered to be the reactive centers of the degradation process involving hydrogen abstraction by a excited \( \alpha \)-carbonyl group from a phenolic group leading to the formation of phenoxy radicals which are able to react with oxygen and to generate quinones and ultimately complex colored products.

In order to better understand the mechanism of light induced degradation of lignin, Kringstad and Lin (1970) have attempted to identify and evaluate the relative importance of photosensitive functional groups, with respect to the yellowing of isolated lignin (MWL) and using model compounds exposed to light of wavelength above 300 nm. They confirmed that phenoxy radicals were formed by hydrogen abstraction by \( \alpha \)-carbonyl compounds in the excited state. Several other mechanisms besides hydrogen abstraction have been proposed to explain lignin photodegradation reactions.

*Norrish Type I reaction* When phenacyl guaiacyl compounds are irradiated with light, the photocleavage of carbon-carbon bonds adjacent to an \( \alpha \)-carbonyl group takes place via a Norrish Type I reaction. However, the Norrish Type I reaction does not occur efficiently in those structures with ether bonds adjacent to the carbonyl group like the model compounds of phenacyl guaiacyl ether.
**α-carbonyl β-O-4 type**  
In this case, photodissociation takes place at the ether bond rather than at the carbon-carbon bonds. The α-carbonyl group appears to absorb light effectively and transfer this energy to the β-aryl ether linkage leading to the cleavage of the ether bond, generating phenolic and carbon radicals. Gierer and Lin (1972) first examined the photoreactivity of O-methylated α-carbonyl β-O-4 dimers, which was later also extensively investigated by Castellan and his coworkers (Castellan, *et al*., 1989; and Vanucci *et al*., 1988). These results showed that the homolytic β-C-O bond cleavage giving phenacyl and guaiacoxyl radicals, is an efficient process leading to the formation of colored oligomeric materials.

**Non-carbonyl α C-O bond cleavage**  
By studying the photochemistry of α (2',4', 6',-trimethyl-phenoxy)-3,4 dimethoxy toluene, Castellan and his research team (1987 and, 1988) found that non-carbonyl α-O-4 bond cleavage was involved in the photochemical degradation of α-O-4 derivatives. A variety of products can be obtained from a homolytic α-O-4 bond cleavage, which leads to reactive species such as free radicals and/or methylene quinones. These quinones ultimately generate oxidizable phenolic derivatives and colored compounds.

**Non-α-carbonyl β-O-4 type**  
Schmidt and Heitner (1993) have proposed the photo-reaction pathways for the group compounds of guaiacylglycerol-β-arylether which include a major ketyl pathway. A ketyl free radical is produced by the benzylic hydrogen abstraction of a peroxyl radical from a guaiacylglycerol-β-arylether group. Ketone and phenoxy radicals are formed by cleavage of the β-arylether bond of the ketyl radical.
The ketyl pathway was first reported by Scaiano, et al (1991), and confirmed by Shkrob, 
et al (1992), and Schmidt and Heitner (1993). Leary (1994) proposed that the ketyl 
pathway accounts for a major portion of the photochemistry of thermomechanical pulp 
(TMP) yellowing.

Participation of singlet oxygen  
Oxygen in its ground state is not able to react 
directly with unsaturated or other electron-rich organic compounds during 
photodegradation. A photosensitizer which can be excited by the radiation energy must be 
present. The (triplet) sensitizer transfers the energy to the ground state oxygen which is 
converted to a reactive singlet molecule. In the oxidative photodegradation of lignin, \( \alpha \)-
carbonyl groups and/or ring conjugated double bond systems function as photosensitizers 
producing excited singlet oxygen. Such a powerful oxidizing and highly diffusible 
species appears to be a suitable candidate for the inducement of photodegradation in a 
solid matrix (Gellerstedt and Pettersson, 1975; Lin and Kringstad, 1970b). A reaction 
mechanism for the lignin degradation with the participation of oxygen, was formulated by 
Brunow and Sivonen (1975). The excited oxygen reacts with phenolic groups to form 
phenoxy radicals which further react to form yellow products. Studies using singlet 
oxygen generators and quenchers suggested the participation of oxygen as an effective 
intermediate in photo-oxidative reaction at wood surfaces (Hon, 1981a).

Several important facts about the photodegradation of lignin have been elicited 
from model compound studies (Hon, 1991a):
1. Phenoxy radicals are readily produced from phenolic hydroxyl groups abstracting hydrogen directly from free phenolic groups.

2. Carbon-carbon bonds adjacent to α-carbonyl groups are photodissociated via a Norrish Type 1 reaction.

3. The Norrish Type 1 reaction does not occur efficiently in those compounds with ether bonds adjacent to the α-carbonyl group. Photodissociation takes place at the ether bonds.

4. Compounds which contain benzoyl alcohol groups are not susceptible to photodissociation, except when photosensitizers participate in the photodegradation of lignin.

5. α-carbonyl groups function as photosensitizers in the photodegradation of lignin.

6. Singlet oxygen is involved in lignin photodegradation when photosensitizers are available.
2-3. Wood protection against photodegradation

Because photo-induced discoloration and deterioration of wood are considered undesirable, much work has been done to protect wood and woody material surface from photodegradation during outdoor applications. On the basis of the most acceptable strategies, one or a combination of the following methods may be adopted to prevent photo-induced degradation (Hon, 1991b).

i. Cutting off the UV light,

ii. Modifying the light absorbing structures present in wood,

iii. Destroying the structures participating in discoloration,

iv. Eliminating oxygen or capturing \( \cdot O_2 \),

v. Scavenging the free radicals formed during photo-exposure.

Modification of the light absorbing structures in wood have been widely studied. Since the \( \alpha \)-carbonyl, conjugated C=C double bond and phenolic hydroxyl groups are the principal chromophoric groups in wood, they must be modified to reduce photodegradation. Acetylation, methylation, hydrogenation and benzoylation efficiently decrease photo-induced oxidation (Gierer and Lin, 1972; and Lin and Kringstad, 1970b). If spruce MWL is first reduced with sodium borohydride, followed by catalytic hydrogenation of the conjugated double bonds, it is completely stable towards UV light
The effect of acetylation on the weathering performance of aspen and fiberboard made of aspen fiber has been studied by Feist, *et al* (1991a and 1991b). The rate of moisture sorption and extent of swelling of the acetylated aspen (at 18% WPG) were reduced compared to untreated controls, while the erosion rate was reduced by 50%, based on the test of accelerated weathering. Dawson and Torr (1992) reported that acetylation could improve the color stability of radiata pine under UV radiation, while the degradation of lignin and carbonyl groups, based on FTIR measurements, was not inhibited. Hon’s work (1995) suggested that acetylation was effective in providing temporary retardation of color change in southern yellow pine during the first 28 days of UV irradiation, although the protection steadily diminished with longer exposure.

Wood finishes (paints and coatings) can effectively protect wood from weathering. The major role of finishes is to build a barrier on wood surface to cut off UV light and water from its surface.

Wood surfaces can be protected against photodegradation by impregnation with wood preservatives containing metal ions of inorganic salts, such as chromic and ferric ions (Chang, *et al*, 1982; and Feist, 1978). The chelate formed between phenolic hydroxyl groups and metal ions may block the reactive centers in wood during photo-exposure. Treatment of wood with chromium trioxide (chromic acid, chromic anhydride), copper, or ammoniacal solutions of these chemicals effectively increases the weathering resistance of wood (Feist, 1979; Feist, 1983; Feist and Williams, 1991; Change, *et al*, 1982; Feist and Hon, 1984; Williams and Feist, 1985; and Jin, *et al*, 1991). A greater preservative content of treated wood generally results in greater resistance to weathering.
and improved surface durability. However, the protective effect of the recently developed preservative ACQ, on weathering is less understood. Wood samples treated with ACQ retarded weathering (Jin, et al, 1991). The chemistry behind this phenomenon is unclear.
Chapter 3

Studies on the photodegradation of wood

3-1. Introduction

As a structural material, wood has been widely used outdoors where it is subject to biological decay and weathering. Various preservatives have been used to prevent wood biodegradation. In fact, certain preservatives can also significantly influence wood weathering (Feist and Hon, 1984; and Jin et. al, 1991). The protective effects of a hexavalent chromium or CCA treatment, have been proposed by several researchers (Feist, 1979; Pizzi, 1980; 1981; and 1982; Chang et. al, 1982; Williams and Feist, 1984; Hon and Chang, 1984; Evans et. al., 1992a; and Mitchell, 1993). The formation of water insoluble, cross-linked chromium-wood complexes may induce several benefits including blocking photoreactive centers, improving dimensional stability and enhancing water repellency, all of which would help retard weathering. The photostabilization of wood-chromium ionic complexes may also occur via a transfer or emission of effective energy from the wood surface, thereby preventing the formation of peroxides. However, currently there are only a few references available related to the influence of AAC and ACQ treatments on wood weathering.

As mentioned in Chapter 1, the negative effect of DDAC treatment on wood weathering was first observed during the field tests of DDAC-treated wood. It was confirmed by accelerated weathering test in the laboratory (Jin et. al., 1991).
negative effects, which included considerable latewood defibration and early wood erosion, was virtually eliminated by formulating DDAC in an ammoniacal copper system, known as ACQ. Jin et al. (1991) have proposed that quaternary ammonium compound (QAC) treatment increased the surface degradation predominately via delignification, and that the cupriammonium DDAC system (ACQ) slowed the lignin degradation. The chemistry behind the phenomena of DDAC and ACQ-treated wood is unclear.

Jin and Preston (1991), and Ruddick and Doyle (1991) have demonstrated that the affinity of QAC towards lignin is much higher than other wood components. Doyle and Ruddick (1994) observed that QACs are more concentrated in the lignin-rich middle lamella region. The mechanism by which QACs are bound to wood involves both ion exchange and ion pairing. It has been proposed that cation ion exchange with protons on carboxylic and phenolic hydroxyl groups may be the dominant mechanism for QAC fixation in wood (Preston et al., 1987; Jin and Preston, 1991). The physical behavior, distribution and fixation of QACs, such as DDAC in wood, might play very important roles in weathering. It is unclear whether this fixation reaction is directly responsible for the change in the weathering behavior of QAC-treated wood, or whether other side reactions with lignin cause the enhanced weathering. Prior to this project, little research has been done on the chemical aspects of QAC fixation in wood. The improved knowledge of the DDAC-wood interaction would be beneficial in developing a better understanding of the weathering chemistry of DDAC-treated wood.

As the QAC fixation in wood is associated with lignin, it is highly probable that the phenomenon of weathering and the mechanism of fixation must be linked. How does
DDAC influence the chemical changes of wood during weathering? The purpose of this study is therefore to investigate both: a) the relationship between QAC treatment, fixation, and the photodegradation of wood and its components; and b) the chemical changes in the wood samples after treatment and following weathering. The nature of the interaction between preservatives and wood, and chemical changes in the photo-exposed treated wood were identified using spectroscopic analysis. It is known that the FTIR spectra of treated and untreated wood samples can be used to identify the changes resulting from the chemical treatment, and that this can then be correlated to the DDAC and ACQ fixation.

For the study of wood surfaces, nondestructive techniques such as FTIR, ESCA, ESR, UV-Vis reflectance spectroscopy, and SEM have successfully provided an insight into the weathering and photo-yellowing of wood and pulp (Hon, 1979a and 1991a; Hon and Feist, 1986; Chang and Hon, 1988; Jin et. al., 1991; Evans et. al., 1992a and 1992b) and preservative fixation (Ostmeyer et. al., 1989; Ruddick and Xie, 1995; Xie et. al., 1996). Among those techniques, FTIR is widely used.

The FTIR technique has four important characteristics which contribute to its usefulness in detecting compositional changes of wood. They are: a) no two molecules have the same infrared spectrum for qualitative analysis; b) there are several characteristic peaks in wood (Characteristic peaks are those that always occur in the same wavelength region. Each of the wood components, cellulose, hemicellulose, and lignin, has its characteristic peak(s)); c) the infrared spectra of mixtures are additive and the absorption
of the key peaks is proportional to the concentration of the chemical studied for kinetic study; and finally d) the IR spectra can be obtained non-destructively.
3-2. Methodology

3-2-1. Photodegradation of DDAC and ACQ-treated wood by weathering and UV irradiation

Preservatives

DDAC and ACQ were the preservatives used in this phase of the research. The DDAC was commercial grade Bardac® 2280 manufactured by Lonza Inc. Bardac® 2280 contains 80% DDAC as the active ingredient, 10% ethyl alcohol and 10% water. A stock solution of 5% ACQ (ammonia:CuO:DDAC:CO₂ = 4:2:1:1.6) was prepared, based on the procedures reported by Archer et. al. (1991). A 5% (CuO) cupric ammonium solution, with the composition of 4NH₃:2CuO:1.6CO₂, was prepared by dissolving 18.12 g basic cupric carbonate in 2/3 of the 250 ml aqueous solution of 10% ammonia and 4.8% ammonium bicarbonate. The solution was then diluted with the remaining ammonium hydroxide solution. The stock ACQ solution was obtained by mixing the ammoniacal copper solution and with the 5% DDAC solution together.

Sample preparation

UV irradiation  Southern yellow pine sapwood sticks with dimensions of 10 mm (tangential) x 10 mm (radial) x 40 mm (longitudinal) (3 - 4 annual rings) were softened using vacuum impregnation in distilled water, and then microtomed along the longitudinal x tangential surface. Various earlywood sections approximately 35, 40, 45, 50, 60, 70, 80, 90 and 100 μm (in thickness) were prepared. After being air-dried, these
sections were soaked in 2.5% solutions of either DDAC or ACQ (ammonia:CuO:Quat = 4:2:1) for 3 hours. The preservative uptake ranged from 0.2 to 0.3% for DDAC and 0.4 to 0.6% for ACQ (on an air-dry weight basis). Four untreated control samples, 40, 50, 70 and 90 μm in thickness, were prepared for comparison with the treated samples.

**Natural weathering** Southern yellow pine sapwood sticks with the dimensions as above were used. The earlywood sections approximately 35, 40, 45, 50, 55, 60, 70 and 80 μm thick were prepared for the weathering study. Six replicates of each thickness were used. The treatments were performed by brushing treating solutions of either DDAC or ACQ (ammonia:CuO:Quat = 4:2:1) onto the surface of the wood section which faced the sunlight.

**Holocellulose** The holocellulose from southern yellow pine was prepared using single stage addition chlorite holocellulose technique (Wise *et al.*, 1946). Wood meal (40 mesh) which had been extracted with benzene - 95% ethanol (2:1) was digested in a mixture of sodium chlorite and buffer solution and shaking at 50°C for 30 hours. Holocellulose was obtained after washing the digested wood meal with 1% acetic acid and then acetone. A KBr disc of holocellulose was prepared for the FTIR measurement.

**DDAC fixation** The DDAC treatments of wood samples were performed by soaking the microtomed earlywood sections of 45 μm in DDAC solutions (0%, 2.5%, 5%, and 10%) for 2 hours. The samples were then air-dried and fastened to FTIR sample holders for the FTIR measurements.
**ACQ fixation**

Both earlywood sections (50 μm) and cellulose (analytical grade filter paper) were used in this experiment. The treatments were conducted by soaking the wood sections or cellulose in treating solution for 2 hours (Table 3-2-1). The FTIR spectra of wood sections were recorded directly from FTIR sample holders, while those of cellulose were recorded using a cellulose-KBr compressed disc.

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Table 3-2-1. The treatments of wood sections and cellulose.

<table>
<thead>
<tr>
<th>Treating solutions</th>
<th>3.33% NH₃ as CuCO₃ in NH₄OH</th>
<th>1.67% CuO as CuSO₄ in NH₄OH</th>
<th>1.67% CuO as CuSO₄</th>
<th>1.67% CuO as 2.5% ACQ NH₄OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>wood</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>cellulose</td>
<td>✓</td>
<td>✓</td>
<td>—</td>
<td>✓</td>
</tr>
</tbody>
</table>

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**Sample exposure**

*Weathering* All the samples were fixed onto the sample holders (the same size as FTIR slides, 110 x 50 mm with an opening of 25 x 10 mm) and placed on two plywood
boards. They were exposed outdoors horizontally with one surface facing the sun. The weathering was conducted during July and August of 1992, for a total period of 35 days between the hours of 5:00 am to 9:00 pm (18 sunny days, 6 cloudy days and 11 partially sunny days). Special care was taken for the sample exposure. During the days when it rained, the sample boards were taken indoors to avoid the leaching of wood substance from samples by rain action. The sample boards was kept indoors at night-time.

Artificial UV irradiation Wood samples were placed in pyrex petri dishes and irradiated with a medium pressure quartz mercury lamp (450 watts) in a pyrex cooling well in a photoreactor chamber which was operated at room temperature (25°C).

Leaching

Wood samples which had been either weathered for 35 days, or UV irradiated for 6 days, were divided into two groups one of which was washed with distilled water and the other was washed with 2% sodium hydroxide solution. The filtrates of each of the samples were collected for UV-Vis spectroscopic analysis, and the residues were retained for FTIR measurements. The DDAC-treated and the untreated wood sections fell apart, after being washed with 2% sodium hydroxide solution. The FTIR spectra of those samples were recorded using a KBr disc.

Spectroscopic analysis

All the FTIR measurements were done using a Perkin-Elmer FTIR 1600 series instrument and the spectra were recorded in the range of 4400-450 cm⁻¹. The UV-Vis spectra were recorded in the ultraviolet-visible range with a Varian Cary13 UV-Vis
spectrophotometer. The IR spectra of the artificial weathered samples (provided by CSI) were recorded using KBr discs containing 250 mg of KBr and 1 mg of wood which was taken from the weathered surface.

**Artificial UV irradiation** FTIR spectra were recorded at four stages: a) before treatment; b) after treatment but before irradiation; c) after 28 hours irradiation; and d) after 6 days irradiation. The wood samples were fixed onto sample holders and directly examined using FTIR.

**Weathering** FTIR spectra were recorded at the following stages: a) untreated and unweathered; b) after treatment but before weathering; and c) weathered. The wood samples, which were fixed on sample holders, were directly examined using FTIR.

3-2-2. Photodegradation of DDAC, DMBC, ACQ, and CCA treated wood by exposure to sunlight

**Preservatives**

The following treatment were used in this phase of the study: DDAC, dimethylbenzylcocoammonium chloride (DMBC), ACQ (ammonia:CuO:DDAC = 4:2:1), and CCA. DDAC was a commercial grade Bardac® 2280 as described in the section 3-2-
1. DMBC (Arquad® DMBC-80) provided by AKZO Chemicals Inc contained 80% DMBC as the active ingredient, 10% ethyl alcohol and 10% water. A stock solution of 5% ACQ (ammonia:CuO:DDAC:CO₂ = 4:2:1:1.6) was used to prepare the ACQ solutions. CCA (type C) working solutions were prepared from a concentrated stock solution of 50% and the concentration were measured using an Asoma X-ray analyzer.

Sample preparation

100 pieces of air-dried southern yellow pine sapwood sticks with the dimensions of 12 mm (tangential) x 12 mm (radial) x 40 mm (longitudinal) (3-4 annual rings) were cut from the same piece of lumber. Those wood sticks were divided into five groups and treated by vacuum impregnation with distilled water (control), DDAC, DMBC, ACQ and CCA solutions, respectively. The representative blocks were then microtomed along the longitudinal x tangential surface to produce earlywood sections [40 mm (L) x 12 mm (T) x 50 μm (R)] for weathering and FTIR measurements. Other treated wood blocks were microtomed with a longitudinal x tangential surface [40 mm (L) x 15 mm (T) x 5 mm (R)] were microtomed for UV-VIS reflectance colorometric measurements. Three replicates were used for FTIR measurements. The treating solution concentrations are listed in Table 3-2-2.

Prior to treatment, wood samples were randomly selected for the determination of the moisture content of southern yellow pine sapwood by the oven-drying method. The preservative uptakes (Table 3-2-3) were calculated on the basis of the oven dried wood weight by excluding moisture content from air-dried wood.
Table 3-2-2. The preservatives used in this experiment.

<table>
<thead>
<tr>
<th>Preservatives</th>
<th>0.25%</th>
<th>0.5%</th>
<th>1%</th>
<th>2%</th>
<th>2.5%</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDAC</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>DMBC</td>
<td></td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>CCA</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>ACQ</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

Table 3-2-3. The preservative uptakes (weight of preservative (mg) in one gram wood).

<table>
<thead>
<tr>
<th>Preservatives</th>
<th>0.25%</th>
<th>0.5%</th>
<th>1%</th>
<th>2%</th>
<th>2.5%</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDAC</td>
<td>3.9</td>
<td>—</td>
<td>14.3</td>
<td>32.1</td>
<td>38.8</td>
</tr>
<tr>
<td>ACQ</td>
<td>3.8</td>
<td>8.3</td>
<td>16.8</td>
<td>32.3</td>
<td>—</td>
</tr>
<tr>
<td>CCA</td>
<td>4.1</td>
<td>8.3</td>
<td>17.4</td>
<td>35.2</td>
<td>—</td>
</tr>
<tr>
<td>DMBC</td>
<td>N/A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Sample exposure

All samples were placed in 54 pieces of Pyrex glass petri dishes, which were fixed on wood boards and exposed outdoors horizontally, with one surface facing the sun. The weathering was conducted in the summer of 1993 in Vancouver, British Columbia, for periods of 7, 14, 21, 28, and 35 days. The weather conditions are showed in Table 3-2-4.

Table 3-2-4. Weather conditions during the exposure of wood samples in Vancouver, 1993.

<table>
<thead>
<tr>
<th>Exposure period (day)</th>
<th>sunny</th>
<th>raining</th>
<th>cloudy</th>
<th>sunny/cloudy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-7</td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>8-14</td>
<td>6</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15-21</td>
<td>4</td>
<td>0</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>22-28</td>
<td>7</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>29-35</td>
<td>6</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

Spectroscopic analysis

FTIR and UV reflectance spectra were recorded for unexposed and exposed samples. They were attached to FTIR sample holders and directly examined using a
Perkin-Elmer 1600 series FTIR with purging the sample cavity with dry air. The sensitivity of the instrument was 8 cm\(^{-1}\). All the spectra were recorded with 64 scans in the range of 4000-450 cm\(^{-1}\) with 20% transmittance. The UV reflectance spectra were recorded in the UV-VIS range with a Varian Cary13 UV spectrophotometer, equipped with a reflectance accessory.

**Leaching**

After outdoor exposure for 35 days, the various treated and untreated wood samples were oven-dried at 103°C and kept in a desiccator over CaSO\(_4\) before weighing and leaching. For water leaching, the wood samples were soaked in distilled water and placed in an ultrasonic bath for 6 hours followed by twice washing with distilled water for 10 minutes two soaking periods in the bath. The washed samples were oven-dried and weighed. The samples were then leached with 2% sodium hydroxide solution using the same procedure, except that the ultrasonication time was 3 hours, instead of 6 hours. After sodium hydroxide leaching, the samples were washed with distilled water three times.

**3-2-3. Effect of methylation**

**Preparation of wood sections**

Southern yellow pine sapwood blocks with dimension of 13 mm (tangential) x 28 mm (radial) x 26 mm (longitudinal) (3-4 annual rings) were softened using vacuum
impregnation in distilled water. The softened blocks were then microtomed along the longitudinal x tangential surface to produce earlywood sections [26 mm (L) x 13 mm (T) x 50 μm (R)] with very few or no resin canals.

**Generation of diazomethane**

Diazomethane was generated according to the method described by Browning (1967). A 45 ml aliquot of diethyl ether and 5 g diazald (purchased from Aldrich Chemical Co.) were placed in a 125-ml dropping funnel which was fitted to a 150-ml Erlenmeyer vacuum flask containing 10 ml 95% ethanol, 5 g potassium hydroxide and 8 ml distilled water. A inlet tube, which was connected to a nitrogen tank, was inserted into the solution in the Erlenmeyer flask and the outlet hooked to a glass tube leading to the second flask containing 75 ml diethyl ether. The receiving flask was connected to a 50-ml test tube with glass tubing. Both receiving flasks were cooled in an ice-salt bath at -20°C (mixture of 1000 g ice and 330 g NaCl salt). Diazald solution was slowly added into the alkali solution and the diazomethane was generated instantly and purged with nitrogen gas to the receivers.

**Methylation of wood sections**

The wood sections were air-dried at 50°C for 2 hours to a moisture content of 4.8%, after which 2.322 g of wood sections were methylated according to the method described by Browning (1967, pp753). Wood sections were added to 70 ml freshly generated diazomethane-diethyl ether solution and left to soak for several hours, after which the solvent color faded. The solvent was replaced with fresh diazomethane diethyl
ether solution and the reaction was allowed to stand overnight. The above methylation process was repeated. More diazomethane was added to the treating solution by purging diazomethane with nitrogen gas and trapping it in diethyl ether cooled at -20°C. The treating mixture was allowed to stand for an additional 24 hours, and the solution retained its yellow colour indicating that excess diazomethane was present. Methylated wood was removed from the diethyl ether and dried at 50°C for 2 hours. The unmethylated control samples were soaked similarly in the ether solvent as described above. The moisture content of the methylated and unmethylated wood sections after drying was 1.2%. All the wood samples were kept in a desiccator prior to photo-exposure.

**DDAC treatment**

Twenty wood sections were soaked for 2 hours either in 40 g distilled water or DDAC solution. The concentrations of the DDAC treating solutions were 2.5% and 5% DDAC. The solution was evacuated during treatment to remove air bubbles. Excess liquid on the sample surface was removed with Kimwipes® tissue. Five wood sections with similar weight and transmittance energy levels were carefully selected from each treatment.

**UV radiation and FTIR measurements**

All wood samples were attached to FTIR holders with an circular opening of 15 mm in diameter. The sample holders were randomly placed in a circle, 25 cm from the medium pressure quartz mercury lamp (450 watts) which was equipped with a quartz cooling well in a photoreactor chamber and operated at room temperature (25°C). The
exposure periods were 10 and 20 hours. All the FTIR measurements were done as described in section 3-3-2. The wood samples were examined at three stages: a) before irradiation; b) after 10 hours irradiation; and c) after 20 hours irradiation.
3-3. Results and discussion

3-3-1. Photodegradation of DDAC and ACQ-treated wood by weathering and UV irradiation

The advantages and limitations of using FTIR technique to study wood photodegradation

Wood surfaces undergo rapid photodegradation on exposure to weather. FTIR has been widely used to study the chemical changes on the wood surfaces. In transmitted FTIR, the resolution is dependent upon both the sample preparation procedure and the sensitivity of the instrument. The traditional method of transmittance FTIR uses a KBr disc or mull of a powdered sample. This approach for studying surface weathering is limited since destructive sampling is required and the same sample cannot be used for repeated measurements. Chemical changes can also occur during sample grinding. In addition, the variation of sampling depth from the weathered surface for examination by FTIR can provide misleading results. For example, the IR spectra (using KBr disc) of ACQ-treated wood after 800 and 1600 hours of weathering showed similar chemical changes (Figure 3-3-1), which didn’t reflect the anticipated greater chemical changes for the sample after 1600 hours weathering. The reason for this was taking samples at different thickness.

In reflectance IR, such as DRIFT (diffuse reflectance infrared Fourier transform), FTIR-IRS (external reflection Fourier transform infrared spectroscopy), or MIRIR (multiple internal reflectance infrared), the same spot on the sample can be monitored during the entire weathering process without surface destruction (Hon and Chao, 1988).
Unfortunately, reflectance IR can not be used to study the depth of light penetration, since the detection of the chemical changes at softwood surfaces by a FTIR-IRS is limited to a depth of approximately 0.13 to 2.15 μm (Zavarin et al, 1991). Evans et al (1992a) reported that after short term natural exposure there was substantial delignification in the surface 1-2 μm of wood. In addition, sunlight can penetrate wood up to 75 μm in depth. Therefore, it is difficult to evaluate the extent of weathering deterioration using FTIR-IRS. The surface roughness also influences the spectral resolution. It has been reported that the longer the exposure time, the poorer the resolution of the DRIFT spectra, due probably to the roughening of wood surface caused by degradation (Hon and Chao, 1988). By monitoring weathering in wood sections of different thickness with transmittance FTIR, the limitations of reflectance and transmittance (KBr disc) methods for measuring changes in wood during photo-exposure can be overcome. This technique allows directly recording the FTIR spectra on the same spot of the samples throughout an experiment. The changes in chemical composition in samples of varying thickness, after exposure to weathering or UV light, can provide information on the depth of photodegradation reactions below the wood surface.

**Fixation of DDAC and ACQ**

The FTIR spectra of an untreated control, 2.5% DDAC, 10% DDAC and 2.5% ACQ soak-treated wood sections (unirradiated) are shown in Figure 3-3-2. The major differences in absorption intensities occurred in the fingerprint region relating to peaks at
Figure 3-3-1. FTIR spectra (KBr) of the surface layer of ACQ treated wood: a) before weathering, and after weathered for b) 800 hours and c) 1600 hours.

Figure 3-3-2. Effect of DDAC and ACQ soak treatment on the infrared spectra of thin EW sections (40 µm in thickness).
1720-1740, 1645-1660, 1510 and 1315 cm$^{-1}$. The assignments of these peaks are listed in Table 3-3-1 (Herbert, 1972; Evans, 1992; and Hon, 1986). The peak at 2856 cm$^{-1}$, which was absent on the spectrum of the untreated control, appeared following DDAC and ACQ treatments. It is associated with C-H stretching in QAC and related to the -CH$_3$ attached to the central nitrogen. It matches that found in the IR spectrum of DDAC (Figure 3-3-3) obtained using polyethylene (PE) as the background. The spectra of both DDAC- and ACQ-treated wood showed decreases in peak intensities and peak splitting at 1510 and 1645-1660 cm$^{-1}$ while the absorbance at 1720-1740 cm$^{-1}$ decreased in the ACQ-treated samples. These changes suggested that various chemical and physical interactions between the preservatives and wood components have taken place.

The absorption at 1510 cm$^{-1}$ is a characteristic peak of lignin due to the C=C stretching vibrations of the aromatic ring present in lignin. This peak usually appears at 1515-1500 cm$^{-1}$ depending on the ring substituents. The decrease in intensity and splitting of this peak in both ACQ and DDAC-treated samples implied that the substituents of the aromatic rings have been changed by the chemical bonding of wood-preservatives. This was also indicated by a reduction in the peak intensity at 1425 cm$^{-1}$ in the both ACQ and DDAC-treated samples. The absorption peak at 1425 cm$^{-1}$ is assigned to an aromatic skeleton vibration, a ring stretching mode coupled with C-H deformation, which is sensitive to the nature of ring substitutes. The absorption peak at 1600 cm$^{-1}$ became more intense following DDAC and ACQ treatments. The strong 1600 cm$^{-1}$ absorption peak arises from aromatic skeleton vibration and COO$^-$ antisymetrical stretching vibration. The increase in the intensity of the 1600 cm$^{-1}$ absorption peak and the decrease in the intensity
Table 3-3-1. The assignments of absorption peaks in IR spectra of southern yellow pine.

<table>
<thead>
<tr>
<th>Fr. (cm(^{-1}))</th>
<th>Group and class</th>
<th>Assignments &amp; remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>2860</td>
<td>OH in wood</td>
<td>OH stretch</td>
</tr>
<tr>
<td></td>
<td>-CH(_3) attached to O &amp; N</td>
<td>CH stretch</td>
</tr>
<tr>
<td>1720-40</td>
<td>C=O in unconj. ketones</td>
<td>C=O stretching</td>
</tr>
<tr>
<td></td>
<td>aldehydes &amp; carboxyl</td>
<td>same</td>
</tr>
<tr>
<td>1645-60</td>
<td>C=O in para-OH substituted</td>
<td>same</td>
</tr>
<tr>
<td></td>
<td>aryl ketone, quinone</td>
<td>H-O-H deformation.</td>
</tr>
<tr>
<td></td>
<td>? H(_2)O absorbed in carbohydrates</td>
<td>C=C stretching</td>
</tr>
<tr>
<td></td>
<td>C=C in alkenes, etc.</td>
<td>aromatic skeletal vibrations</td>
</tr>
<tr>
<td>1600</td>
<td>C=C in aromatic ring in lignin</td>
<td>COO(^-) antisymetrial stretch</td>
</tr>
<tr>
<td></td>
<td>COO(^-)</td>
<td>same</td>
</tr>
<tr>
<td>1510</td>
<td>same</td>
<td>same</td>
</tr>
<tr>
<td>1425</td>
<td>C=C in aromatic ring</td>
<td>same</td>
</tr>
<tr>
<td></td>
<td>CH(_2) in carbohydrates</td>
<td>CH(_2) bending</td>
</tr>
<tr>
<td>1370</td>
<td>C-H in all components in wood</td>
<td>C-H deformation (bending)</td>
</tr>
<tr>
<td>1315</td>
<td>CH(_2) in cellulose</td>
<td>CH(_2) wagging</td>
</tr>
<tr>
<td>1267</td>
<td>CO in lignin and hemic.</td>
<td>guaiacyl ring breathing with CO-stretching</td>
</tr>
<tr>
<td>1162</td>
<td>C-O-C in cellulose</td>
<td>antisym. bridge oxygen stretching</td>
</tr>
</tbody>
</table>

of the peaks at 1510 and 1425 cm\(^{-1}\) can be interpreted due to progressive substitution of the aromatic ring (Hergert, 1971). Elofson (1957) noted that the absorption at 1510 cm\(^{-1}\) was completely absent in hexamethylbenzene. In a study on the delignification of
Eucalyptus regnans, Mitchell et al (1965) proposed that the occurrence of a broad peak near 1600 cm\(^{-1}\) is mainly due to a shift in the carboxylate peak from 1730 cm\(^{-1}\), as a result of salt formation associated with carboxylic group. The intensity of absorption at 1645-1660 cm\(^{-1}\), assigned to the \(\alpha\)-C=O conjugated with a para-hydroxylphenyl group, decreased following the DDAC and ACQ treatment. This suggested a reduction in the phenolic hydroxyl content. Hergert (1971) stated that the addition of an OH group at the para position of the acetophenone molecule caused a further shift from 1685 cm\(^{-1}\) to 1645 cm\(^{-1}\) as a result of the electron-donating character of the para-phenolic hydroxyl group. The acetylation of coniferylaldehyde nullified the effect of the para-phenolic hydroxyl group by increasing the frequency from 1652 to 1670 cm\(^{-1}\) (Hergert, 1971). The decrease of the peak intensity due to phenolic hydroxyl group following DDAC and ACQ treatment, suggested that an interaction of the hydroxyl group with DDAC and ACQ had taken place. The FTIR results confirmed that the cation ion exchange took place between DDAC and the protons in the carboxylic acid and phenol in wood (Jin and Preston, 1992 and Doyle, 1995). The near constancy of the peak at 1162 cm\(^{-1}\) before and after DDAC treatment indicated that cellulose was less affected. The FTIR spectra of ball-milled wood meal (BMWM) samples showed that the ratio of the peak height of all lignin peaks to a cellulose peak at 895 cm\(^{-1}\) (internal reference) decreased after being treated with DDAC (Figure 3-3-4). The most significant changes took place with concentrations of up to 0.5% DDAC, while further changes as the DDAC concentration increased to 2.5% were much smaller. This suggested that the available reaction sites in BMWM were mostly saturated following treatment with 0.5% DDAC.
Figure 3-3-3. The FTIR spectrum of DDAC obtained using polyethylene film as the background.

Figure 3-3-4. The FTIR spectral peak height ratio of ball mill wood meal treated with DDAC, a) 0%; b) 0.5%; c) 2.5%.
Figure 3-3-5a. The influence of different treatments of
a) untreated control, b) 2.5% ACQ, and c) CuCO₃-NH₃,
on the absorption peak of wood sections at 1315 cm⁻¹.

Figure 3-3-5b. The influence of different treatments
of a) CuSO₄-NH₃, b) CuSO₄, and c) NH₃ on the
absorption peak of wood sections at 1315 cm⁻¹.
The substantial decreases in intensities of the FTIR peaks at 1720-1740, 1510 and 1425 cm$^{-1}$ and the increase in intensity of the peak at 1600 cm$^{-1}$ in ACQ-treated samples, suggested that complexes were formed between ACQ and functional groups (such as carbonyl, carboxyl, phenolic hydroxyl and aldehyde) present in wood. The formation of a diammine-copper (II) complex with two guaiacyl units in wood has been suggested on the basis of observations reported by Xie et al (1996) in which reactions with vanillin, a lignin model compound, were studied.

The absorption peak at 1315 cm$^{-1}$ also became weaker following ACQ treatment (Figure 3-3-2). This peak corresponds to the CH$_2$ wagging in cellulose. This phenomenon was found to be related only to Cu-NH$_4$OH treatment of wood (Figure 3-3-5a). There were no changes in the spectra of both CuSO$_4$- NH$_4$OH, CuSO$_4$ and NH$_4$OH treated wood (Figure 3-3-5b). Later results showed this peak increased with an increase in UV irradiation time. This change could be related to the carbonate ion in wood. The association of the change in absorption peak at 1315 cm$^{-1}$ with ACQ treatment indicated that cellulose was involved in the ACQ fixation in wood.

**Effect of ACQ and DDAC on wood photodegradation by natural weathering.**

It has been suggested that UV irradiation of wood results in (a) formation of carbonyl groups and quinones (colored matter), (b) destruction of benzene rings and (c) demethoxylation (Hon, 1991a). These findings in untreated wood and milled wood lignin (MWL) have been proven using FTIR to monitor the changes of characteristic absorption peaks during wood photo-irradiation (Hon, 1988; and Hon and Chao, 1988).
The peaks in the “finger print region” (1800-1100 cm\(^{-1}\)) have been selected by most researchers for the study of wood photodegradation since they can be related to specific wood components and wood oxidation. With weathered wood, this study focused on the changes of absorption peaks at 1720-1740, 1645-1660, 1600, 1510, 1267 and 1162 cm\(^{-1}\), which reflected the vibrations of benzene rings and major functional groups present in lignin and carbohydrates. As shown in Table 3-3-1, the absorption at 1720-1740 cm\(^{-1}\) is related to the C=O group stretching vibrations in aldehydes, unconjugated ketones, esters and carboxylic acids. The 1645-1660 cm\(^{-1}\) peak is considered to be associated with alpha-C=O (conjugated aryl ketones), unconjugated C=C groups and water. Absorptions at 1600 and 1510 cm\(^{-1}\) represent benzene ring skeletal vibrations. The characteristic absorption of guaiacyl ring breathing with CO-stretching is at 1267 cm\(^{-1}\). The antisymmetric bridge oxygen stretching vibration of C-O-C in cellulose is attributed to the strong absorption at 1162 cm\(^{-1}\).

The IR spectra of untreated, DDAC and ACQ-treated earlywood sections, before and after weathering are shown in Figures 3-3-6, 3-3-7, and 3-3-8 respectively. The most obvious differences in these spectra are the decrease in intensity or absence of absorption peaks at 1267, 1510 and 1600 cm\(^{-1}\), and the increases of absorbance at 1720-1740 cm\(^{-1}\) following weathering. Similar results were also observed from the spectra of wood samples with different thicknesses (which will be discussed in the section on sample thickness). The changes in peaks at 1510, 1600 and 1267 cm\(^{-1}\) are related to delignification and demethoxylation, which contribute to the discoloration at wood surfaces during the generation of new chromophoric groups, such as carbonyl-containing compounds and quinones. Evidence for this can be found in the increase in absorbance at
1720-1740 cm\(^{-1}\) and the visible color changes. These findings support the generalized view that the photodegradation of wood is oxidative in nature, as discussed by Hon and Feist (1986; and Hon, 1988) using FTIR and ESCA. These studies also noted that cellulose degradation was less affected by the weathering, since the intensity of the peak at 1162 cm\(^{-1}\) did not change greatly with weathering for all the wood samples.

**Delignification** The delignification of weathered wood can be easily observed from the changes in the characteristic peaks of lignin at 1600 and 1510 cm\(^{-1}\) and the peak associated with lignin at 1267 cm\(^{-1}\). As shown in the IR spectra of untreated control, DDAC- and ACQ-treated wood, 40 μm in thickness, after 35 days of weathering, the absorption peak at 1600 cm\(^{-1}\) disappeared for both untreated samples (Figure 3-3-6) and DDAC-treated sample (Figure 3-3-7), whereas they became stronger for ACQ-treated sample (Figure 3-3-8). The peaks at 1510 and 1267 cm\(^{-1}\), were not detected for DDAC-treated sample, were very weak in intensities for the control, and relatively weak for ACQ-treated sample, suggesting the removal of lignin. DDAC obviously accelerates the delignification. ACQ was capable of retarding the delignification.

**Formation of carbonyls** The spectra in Figure 3-3-6 and 3-3-7 exhibited an increase in the absorption intensity at 1720-1740 cm\(^{-1}\), indicating the formation of carboxylic and carbonyl groups. Both untreated control and DDAC-treated samples reached a similar degree of oxidation, based on the changes in the intensity of the peaks at 1720-1740 cm\(^{-1}\).
Figure 3-3-6. The FTIR spectra of untreated wood sections (45 μm): a) before weathering and b) after weathering for 35 days.

Figure 3-3-7. The FTIR spectra of DDAC-treated wood sections (45 μm): a) before weathering and b) after weathering for 35 days.
Figure 3-3-8. The FTIR spectra of ACQ-treated wood sections (45 μm): a) before weathering and b) after weathering for 35 days.
The peaks were broadened about 40 cm\(^{-1}\) after weathering, suggesting that various carbonyl containing compounds were formed and that all the wood components might be involved in the photodegradation. The broadening of peaks at around 1730 cm\(^{-1}\) in the IR spectra of DDAC-treated samples was greater than that in the spectra of controls. In addition, several shoulders associated with peaks in the region of 1800-1700 cm\(^{-1}\) appeared after exposure to weathering, which indicated that different types of carbonyls were formed during weathering. After 35 days of weathering, the absorption intensity of DDAC-treated wood in the region of 1645-1660 cm\(^{-1}\) was weaker than that of untreated control. This suggested that the conversion of phenolic hydroxyl groups and α C=O groups in DDAC-treated wood was higher than that in the untreated control. The bonding of DDAC to phenolic hydroxyl groups in lignin might be responsible for this rapid conversion. As mentioned before, the absorption in the region 1645-1660 cm\(^{-1}\) is assigned mainly to the α-C=O conjugated with a para-hydroxylphenyl group, and also possibly to quinone vibrations. The changes in the intensity of absorption peaks in this region suggested the possibility of less quinones formed in DDAC-treated wood than in controls during weathering.

**Roles of ACQ**

The spectra of the samples brush-treated with ACQ after 35 days of weathering, did not show significant changes in the intensities of the peaks at 1720-1740, 1600 and 1267 cm\(^{-1}\) (Figure 3-3-8). This observation provided direct evidence that ACQ inhibited wood photodegradation, in agreement with Jin and coworkers’ finding (1991). It is proposed that Cu(II) plays the major role in prohibiting wood photodeterioration. The light resistance of ACQ-treated wood likely results from Cu(II) chelating with functional
groups in wood, such phenolic and methoxyl from guaiacyl unit, and carboxyls. These chelates can photostabilize wood. Evans et. al. (1992a) postulated that photostable lignin complexes were responsible for the enhanced weathering resistance of wood by chromium trioxide treatment.

The spectra of ACQ-treated samples in Figure 3-3-8 show that the absorption peak around 1650 cm⁻¹ has disappeared after 35 days of weathering. Since conjugated alpha-carbonyls, and quinone vibrations contribute to the absorption in this region, these reductions indicate that ACQ doesn’t inhibit some photoreactions involving functional groups such as alpha-carbonyls in wood components. The alpha-carbonyl is thought to be the most reactive chromophore in wood to. The decrease of alpha-carbonyl content after 35 days of weathering might imply that the carbonyls are partially transformed to carboxyls by oxidation and partially to hydroxyl groups by reduction, since the photoreactions of alpha-carbonyls group in an aromatic compound can undergo both oxidation and reduction. The disappearance of peaks at around 1650 cm⁻¹ also suggests that no detectable photoproducts, such as conjugated alpha-carbonyl groups and quinones, were generated or accumulated by 35 days of weathering. This observation could be related to the deterioration and formation of these functional groups during the weathering, indicating the inhibition of photo-oxidation of wood by the presence of ACQ.

Delignification in ACQ-treated wood was not very extensive, although the intensity of peaks at 1510 and 1267 cm⁻¹ were weakened, the peak at 1600 cm⁻¹ remained strong. There are two reasons for this limited degradation. Firstly, the samples were treated by brushing and although a relatively concentrated solution (5%) was used, complete penetration and complexation of Cu(II) with lignin was not achieved. In
addition, UV light can penetrate up to 50-70 μm into wood, therefore degradation can occur in areas where ACQ retention is insufficient.

**Effect of ACQ and DDAC on wood photodegradation by artificial UV irradiation**

The FTIR spectra of an untreated sample before and after UV exposure through pyrex are shown in Figure 3-3-9. Noticeable changes included the absorption peaks at 1720-1740, 1600, 1510 and 1267 cm\(^{-1}\) which were due to benzene rings and the functional groups present in lignin and carbohydrates. The FTIR spectra of a DDAC-treated sample (Figure 3-3-10) showed similar changes to that of the untreated control. The intensity of absorption peaks at 1720-1740 cm\(^{-1}\) increased and the peaks gradually became broader with increasing duration of UV irradiation, whereas the intensity of absorptions at 1600, 1510 and 1267 cm\(^{-1}\), decreased. Both Figures 3-3-9 and 3-3-10 show the weakening and splitting of the peak at 1510 cm\(^{-1}\) with UV light irradiation. This revealed that the delignification took place via both destruction and substitution of benzene rings. The decrease of absorption intensity at 1267 cm\(^{-1}\) may be caused by not only demethoxylation, but also by destruction of aromatic rings, since the destruction of the guaiacyl structure is directly related to the destruction of aromatic ring structure.

A comparison of the photostability of DDAC-treated wood and untreated control samples revealed that after 6 days of UV exposure the carbonyl absorption in the IR spectrum of the DDAC-treated sample was slightly stronger than that in the spectrum of the untreated wood. This indicated that DDAC treatment enhanced the carbonyl formation, an index of the photooxidation of wood, but not as significantly as the effect on delignification. The lignin peaks at 1510 and 1267 cm\(^{-1}\) were much weaker for
DDAC-treated wood (Figure 3-3-10, d) compared to those of the untreated controls (Figure 3-3-9, b), indicating that DDAC accelerated delignification. This observation further confirmed that the reduced weathering resistance of DDAC-treated wood was caused by the enhanced photodegradation. These results supported the proposal that the consequences of photo-induced oxidation and degradation of wood included both the formation of carbonyl containing compounds and the modification and destruction of benzene rings. These photoproducts, such as carboxylic acids, carbonyl and quinones, function as new chromophoric groups which in turn can continue to induce the color changes at the wood surface. Thus, a sharp change in color could be seen after a certain period of irradiation.

The spectra of a wood section treated with ACQ and subsequently irradiated with UV light are shown in Figure 3-3-11. It seems that all the major peaks mentioned above have hardly changed even after six days of irradiation. This is in agreement with the observations reported by Jin et. al. (1991) and the natural weathering results discussed earlier. After six days exposure, the absorption peak around 1650 cm\(^{-1}\) disappeared but the absorption at 1600 cm\(^{-1}\) became more intense. The absorption intensity at 1735 cm\(^{-1}\) slightly increased with UV exposure. The same phenomenon has also been observed from the spectra of other wood sections (of different thickness). This indicates that a certain amount of wood photodegradation occurred in the sample treated with 2.5% ACQ.
Figure 3-3-9. The FTIR spectra of untreated wood sections (50 μm): a) before UV irradiation and b) after UV irradiation for 6 days.

Figure 3-3-10. The FTIR spectra of 2.5% DDAC-treated wood sections (45 μm): a) before UV irradiation, and after irradiation for b) 7 hours, c) 28 hours, and d) 6 days.
Figure 3-3-11. The FTIR spectra of 2.5% ACQ treated wood sections (45 μm): a) before UV irradiation and b) after UV irradiation for 6 days.
The characteristic peak of cellulose at 1162 cm$^{-1}$ had no significant change after six days of UV irradiation for all the treated and untreated samples. The FTIR results of UV-irradiated wood are in agreement with those of naturally weathered wood.

**Physical phenomena**

When wood is exposed to weather or artificial UV light for a relatively short period, changes in color are readily observed. The initial change in the color of wood is usually yellowing after a short exposure to light. Following prolonged exposure (in some cases) the woody materials become white and finally turning to brown (Kringstad, 1969; Feist and Hon, 1984; and Desai, 1968). In the natural weathering experiment, the color changes in the weathered samples revealed that the photodegradation of DDAC-treated and untreated wood occurred at different rate. After 35 days of natural weathering, the DDAC treatment induced whitening of samples while the untreated samples turned yellow. This implies that the weathering of DDAC-treated wood was accelerated by DDAC treatment and reached the whitening stage much faster than that of untreated controls.

Interestingly, the infrared transmittance of DDAC-treated samples increased upon exposure to weather, while that of controls decreased. This was probably due to the transformation of colored materials, loss of gaseous substances, and checking of the thin wood sections. The light color of samples would also tend to increase infrared transmittance. Material loss and check formation due to defibration would also increase infrared transmittance. The accumulation of yellow matter on untreated wood sections may tend to block the transmission of infrared light. The physical changes of weathered
samples in terms of color and infrared transmittance are consistent with the conclusion that treatment with DDAC reduced the natural weathering resistance of wood, and facilitated wood photodegradation.

The DDAC-treated and untreated wood samples irradiated with artificial UV light had no significant change in color after 28 hours irradiation, but yellowed after 6 days of irradiation. In this case, after six days of irradiation of wood, there was no obvious difference in color between DDAC-treated samples and untreated samples, although the FTIR spectra showed changes. Thus, the DDAC-treated sections hadn't reached the whitening stage after six days UV irradiation under these experimental conditions. A comparison of the FTIR spectra of naturally weathered samples (Figure 3-3-7) and UV irradiated samples (Figure 3-3-10) revealed that more lignin remained in the UV irradiated wood than in those naturally weathered. The whitening of DDAC-treated wood by weathering visually reflected the complete or nearly complete removal of lignin, as confirmed by the FTIR results.

After being weathered for 35 days, the coloured material of both DDAC-treated and untreated samples readily dissolved in 2% sodium hydroxide solution. The wood fibers appeared similar to those of bleached pulp. The ACQ-treated samples only partially lost color in the sodium hydroxide solution. The six day UV irradiated sample was bleached by the solution very slowly and the coloured material was completely dissolved. The FTIR spectra (Figure 3-3-12) of wood samples (weathered by 35-day and washed with 2% sodium hydroxide solution) showed that the degree of lignin removed in
Figure 3-3-12. FTIR spectra (KBr) of wood samples leached with 2% NaOH solution: untreated control a) before weathering (45 μm) and b) after weathering; c) DDAC-treated and weathered (50 μm); d) chloride holocellulose.
these samples decreased in the following order: weathered DDAC-wood > weathered control-wood > chlorite holocellulose >> unweathered wood. This ordering was based on the variation in intensity of the absorption peaks at 1510 and 1267 cm\(^{-1}\). This confirmed the results obtained from the weathering experiments. The lignin in weathered wood was soluble in 2% sodium hydroxide solution and partially soluble in water. The extracted fraction showed a UV absorption at 280 nm. This might suggest the fragmentation of lignin during weathering. The residual lignin, remained in the weathered wood (Figure 3-3-6 and 7), might have been oxidized to low molecular weight polymers. The carbonyl containing substances were completely dissolved in the sodium hydroxide solution as the absorption peaks at 1720-1740 cm\(^{-1}\) disappeared with the washing (b and c, Figure 3-3-12), confirming that the color matters arose mainly from carbonyl containing compounds and readily dissolved in alkaline solution.

**Effect of sample thickness**

The extent of the deterioration of wood by weathering depends on both the rate of surface photooxidation and the depth of light penetration. It is thought that the penetration of UV light into wood is between 25 µm to 75 µm (Feist and Hon, 1984). This varies with factors such as wood species, distribution of cells, density and type of wood, (i.e. early-wood, latewood, hardwood, or softwood).

In this study, thin earlywood sections of southern yellow pine sapwood of various thickness were directly exposed to weathering for 35 days. The FTIR spectra of control samples (Figure 3-3-13) showed that the extent of delignification and demethoxylation (based on intensities of peaks at 1510 and 1267 cm\(^{-1}\)) were approximately the same when
samples were thinner than 50 μm. With the increase in sample thickness from 55 to 80 μm, the magnitude of the changes decreased. This demonstrated that weathering or sunlight can directly destroy the earlywood of southern yellow pine to a depth of 50 μm in a period of 35 days.

Figure 3-3-14 showed the effect of sample thickness on the weathering of DDAC-treated wood. Based on the change of intensity of the peak at 1510 cm⁻¹, there was deterioration up to a depth of 80 μm. The decrease of absorbance at 1510 cm⁻¹, caused by 35 days of weathering, was retarded by the increase in specimen thickness (over 55 μm).

Figure 3-3-15 showed the IR spectra of ACQ-treated samples of three different thicknesses. The sensitivity of the IR measurement for ACQ-treated samples was not as good as the other samples. This is consistent with the previously mentioned observation that the presence of ACQ on wood surfaces prevents the penetration of UV light. The extent of delignification in wood by the weathering was reduced when the sample thickness was greater than 45 μm.

The IR spectrum of 35 μm thick untreated latewood section showed that latewood had a much greater weathering resistance than earlywood (Figure 3-3-16): loss of lignin in wood was less severe than for an 80 μm thick earlywood sample, based on the change in the intensity of peak at 1510 cm⁻¹.
Figure 3-3-13. FTIR spectra of untreated wood sections.  
a, c, and e: unweathered, 35, 55 and 80 µm in thickness, respectively;  
b, d, and f: weathered for 35 days, 35, 55 and 80 µm in thickness, respectively.

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Figure 3-3-14. FTIR spectra of DDAC-treated wood sections. 
a, c, and e: unweathered, 35, 50 and 80 µm in thickness, respectively; 
b, d, and f: weathered for 35 days, 35, 50 and 80 µm in thickness, respectively.
Figure 3-3-15. FTIR spectra of ACQ-treated wood sections.
a, c, and e: unweathered, 35, 50 and 80 μm in thickness, respectively;
b, d, and f: weathered for 35 days, 35, 50 and 80 μm in thickness, respectively.
Figure 3-3-16. FTIR spectra of wood sections after weathering for 35 days: a) untreated latewood, 35 µm in thickness, b) untreated earlywood, 80 µm in thickness, and c) DDAC treated early wood, 80 µm in thickness.
Figure 3-3-17. The FTIR spectra of untreated wood sections of different thickness, after UV irradiation for 6 days.

Figure 3-3-18. The FTIR spectra of 2.5% DDAC-treated wood sections of different thickness, after UV irradiation for 6 days.
The spectra of UV irradiated samples, as shown in Figures 3-3-17 and 3-3-18 further confirmed the results obtained from the natural weathering studies. The decrease in absorbance of the peaks at 1510 cm\(^{-1}\) with UV light radiation, was retarded by the increase of the sample thickness for both untreated controls and DDAC-treated samples. Comparison of the FTIR spectra of samples UV-irradiated for 6 days indicated that the lignin peak for any given sample thickness was weaker in DDAC-treated samples than in untreated controls. The absorbance of the peak around 1730 increased proportionally with sample thickness for both irradiated and unirradiated controls (Figure 3-3-19).

![Graph showing absorbance vs. thickness for untreated controls]

Figure 3-3-19. The absorbance of the peak at around 1730 cm\(^{-1}\) for untreated controls.
According to Beer's Law, the concentration of a compound is proportional to its absorbance, which is applied to all the absorption spectra.

\[ A = abc \]

where \( A \) = absorbance; \( a \) = absorptivity, \( b \) = path length; \( c \) = concentration

For solids, such as wood, a useful method of analysis is the internal standard ratio method. In order to quantitatively analyze the changes in the absorption peaks, a typical C-O-C bridge vibration in cellulose at 1162 cm\(^{-1}\) was used as an internal standard (Hon and Feist, 1986; and Segal et. al, 1960) since cellulose is more stable to UV light than lignin and hemicellulose. For comparison between samples, the areas of the peaks of interest were calculated as a ratio to the C-O-C vibration peak area (1162 cm\(^{-1}\)). In this way, the influence of sample heterogeneities, baseline errors, peak area variations and sample preparation, can be reduced. Peak baselines were drawn from the point of transmittance at the beginning of the peak to its end.

The peak areas at 1730 and 1162 cm\(^{-1}\) and their ratios for unweathered and weathered samples are listed in Table 3-3-2. The peak area ratios \( (A_1/A_2) \) of the control, the DDAC, and the ACQ-treated wood samples of the same thickness were initially almost identical before exposure, but were significantly different by day 35 of exposure to weather. Such differences in the \( A_1/A_2 \) ratios from day 0 to day 35, indicated that the rate of carbonyl formation should be DDAC > control > ACQ. The spectrum of the 55 \( \mu \)m thick section for DDAC-treated and that of 50 \( \mu \)m thick section for untreated wood showed the maximum peak area ratio of the peak at around 1730 cm\(^{-1}\) to that at 1162 cm\(^{-1}\) after 35 days exposure to weather (Table 3-3-2).
Table 3-3-2. The relative absorbance ratio of peak at 1730 cm\(^{-1}\) (\(A_1\)) to that at 1162 cm\(^{-1}\) (\(A_2\)) before and after weathering.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Relative absorbance ratio ((R = A_1/A_2))</th>
<th>unweathered</th>
<th>weathered</th>
</tr>
</thead>
<tbody>
<tr>
<td>35 (\mu)m thick</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>0.47</td>
<td>1.66</td>
<td></td>
</tr>
<tr>
<td>DDAC-treated</td>
<td>0.50</td>
<td>1.61</td>
<td></td>
</tr>
<tr>
<td>ACQ-treated</td>
<td>0.45</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>40 (\mu)m thick</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
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<td>1.88</td>
<td></td>
</tr>
<tr>
<td>DDAC-treated</td>
<td>0.61</td>
<td>2.31</td>
<td></td>
</tr>
<tr>
<td>ACQ-treated</td>
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<td>0.89</td>
<td></td>
</tr>
<tr>
<td>45 (\mu)m thick</td>
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<td></td>
</tr>
<tr>
<td>Control</td>
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<td></td>
</tr>
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<td>50 (\mu)m thick</td>
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</tr>
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<td>55 (\mu)m thick</td>
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<tr>
<td>DDAC-treated</td>
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<tr>
<td>ACQ-treated</td>
<td>0.76</td>
<td>1.06</td>
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</tbody>
</table>

It is not clear whether the deeper penetration of UV light for DDAC samples is due to DDAC enhancing mass transfer (via free radicals) or the accelerated defibration
and check formation on the surface, or possibly both. The increase in the rate of
degradation of DDAC-treated wood compared to that of the untreated control has been
further examined using the FTIR quantitative analysis on the UV-irradiated samples.
Both the delignification and demethoxylation rates for DDAC-treated samples were
greater than for the untreated control.

Table 3-3-3. Changes in peak area ratios (using the peak at 1162 cm$^{-1}$ as the internal
standard) in the FTIR spectra of UV irradiated samples.

<table>
<thead>
<tr>
<th>peak (cm$^{-1}$)</th>
<th>treatment</th>
<th>40 μm</th>
<th>50 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>not ird.</td>
<td>6 days</td>
</tr>
<tr>
<td>1730</td>
<td>control</td>
<td>0.39</td>
<td>1.35</td>
</tr>
<tr>
<td></td>
<td>DDAC</td>
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<td></td>
<td>ACQ</td>
<td>0.31</td>
<td>0.45</td>
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<tr>
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<td>control</td>
<td>0.61</td>
<td>0.40</td>
</tr>
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<td>DDAC</td>
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<td>ACQ</td>
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<td>control</td>
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<td></td>
<td>ACQ</td>
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<td>0.96</td>
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</tbody>
</table>
The quantitative analysis results for artificial UV irradiated samples are shown in Tables 3-3-3. The spectra of the samples (both control and DDAC-treated) in 40 μm thick sections showed a maximum absorbance in the 1720-1740 cm\(^{-1}\) region after 6 days irradiation. The difference between the extent of delignification and demethoxylation was similar for untreated controls and DDAC-treated samples at all of the section thicknesses. This suggested that DDAC accelerated the wood photodegradation rate via both delignification and demethoxylation. For ACQ-treated samples, demethoxylation occurred at a greater rate than delignification. As shown in Table 3-3-3, the relative delignification of ACQ-treated sections (50 μm thick) was 11%, which was one fifth of that of DDAC-treated sections (58%) of the same thickness. The relative demethoxylation was 26% for ACQ-treated samples and 50% for DDAC-treated samples. The lower amounts of delignification and carbonyl formation for ACQ-treated wood indicated that the enhanced weathering resistance of wood by ACQ treatment was mainly due to the inhibition of delignification and photooxidation.

A comprehensive summary of both the artificial UV irradiation and weathering experiments may be made by comparing changes in spectra, the peak areas, and the area ratios of the peaks to an internal reference peak, for the ACQ- and DDAC-treated and untreated wood sections. The amounts of delignification, demethoxylation and carbonyl formation in both weathered and UV irradiated wood sections were DDAC > control >> ACQ, based upon changes in FTIR spectra. The agreement of the results from UV irradiated and naturally weathered wood samples suggested that the photochemical reaction in the laboratory can accurately model the natural weathering process. This is supported by the work done by Kimura et al. (1994) and Hon and Chao (1988).
et. al. (1994) have reported that the decrease of the aromatic rings and guaiacyl structures is the same at all wavelengths for unbleached pulp. The changes in the reflectance curves of wood exposed to UV light through a quartz filter, were similar to that through a pyrex filter. The broadening and shoulder formation in the region of the carbonyl absorption suggested that various carbonyl groups had been produced during weathering and UV irradiation in both untreated and DDAC-treated samples. ACQ inhibited wood photodegradation mainly due to the stabilization of lignin by ACQ-lignin complexes. But ACQ did not inhibit some photoreactions, such as those involving functional groups like alpha-carbonyls. Sunlight can directly degrade the earlywood of southern yellow pine to a depth of about 50 μm for untreated wood, and possibly up to 80 μm for DDAC-treated wood, after exposure to weathering for 35 days. DDAC treatment accelerated wood degradation mainly via delignification. Cellulose was degraded by weathering as well as by UV-irradiation much less than lignin. The fixation of DDAC to lignin in wood, likely is one of the principal factors affecting wood photodegradation. The detailed mechanism involved in DDAC-wood photodegradation has yet to be solved.
3-3-2. Photodegradation of DDAC, DMBC, ACQ, and CCA-treated wood by exposure to sunlight

In evaluating the weathered wood, attention was focused on the changes of absorption peaks at 1720-40, 1600, 1510, 1267, and 1162 cm\(^{-1}\) (the assignments of characteristic IR absorption peaks in wood are listed in Table 3-3-1). Quantitative analyses were made on how the carbonyl formation and photodegradation rates of lignin and cellulose changed with the different preservatives, their retention, and increasing exposure time. The intensity and shift of these peaks were also considered, since they could be related to changes in the functional groups and chemical structure of the wood components.

Overview of FTIR Spectra

The IR spectra of untreated earlywood sections and those treated with 0.25% DDAC. 2.5% DDAC, 0.25% ACQ, 2% ACQ, 0.25% CCA, and 2% CCA before and after weathering, are shown in Figures 3-3-20 to 29, respectively. For all of the treated and untreated samples, the intensity of the peaks at 1510 and 1267 cm\(^{-1}\), gradually decreased with weathering, while the intensity of peaks at 1720-1740 cm\(^{-1}\) increased and broadened. These changes were enhanced by 2.5% DDAC treatment (Figure 3-3-22) but not by 0.25% DDAC treatment (Figure 3-3-21), and were slowed by ACQ (Figures 3-3-24 and 3-3-25) and CCA (Figures 3-3-26 and 3-3-27) treatments. The decrease of the peak intensity at 1600 cm\(^{-1}\) with weathering was observable in the spectra of all the samples,
except that treated with 2% ACQ (Figure 3-3-25). By day 7 of weathering, the intensity of peaks at 1510 and 1267 cm\(^{-1}\) was obviously weaker for the 2.5% DDAC treated sample than the others (Figure 3-3-28). After 28 days of weathering, the characteristic peak of lignin, at 1510, was hardly detectable for the 2.5% DDAC treated samples, was very weak for the controls, 0.25% DDAC treated, and 2% DMBC treated, and relatively weak for 0.25% ACQ, and 0.25% and 2% CCA treated samples (Figure 3-3-29). The peaks remained relatively strong for the 2% ACQ treated sample. Considering the peak at 1267 cm\(^{-1}\), it disappeared after 14 days of weathering for the 2.5% DDAC-treated sample (Figure 3-3-22), after 21 days for the DMBC-treated sample, and after 28 days for both the untreated control and 0.25% DDAC-treated samples. These changes at peaks 1510, 1600 and 1267 cm\(^{-1}\) are related to delignification and demethoxylation both of which contribute to photooxidation of the wood surface by generating new chromophoric groups such as carbonyl-containing compounds and quinones. The increase in absorbance at 1720-1740 cm\(^{-1}\) and the color changes are the indications of photooxidation. All the wood samples yellowed during the exposure periods of 7 to 21 days and the yellowing was still observed for all of the samples after 28 days exposure, except for the samples treated with DDAC, which had become bleached. This observation indicated that the DDAC-treated samples had reached a more advanced photo-oxidation stage than the other samples. This is consistent with results obtained from the previous natural weathering study. The intensity of the cellulose peak at 1162 cm\(^{-1}\) did not change greatly with weathering, for both the treated and untreated samples.
Figure 3-3-20. The FTIR spectra of untreated wood sections (50 μm) before and after natural exposure for 7 to 28 days.

Figure 3-3-21. The FTIR spectra of 0.25% DDAC-treated wood sections (50 μm) before and after natural exposure for 7 to 28 days.
Figure 3-3-22. The FTIR spectra of 2.5% DDAC-treated wood sections (50 μm) before and after natural exposure for 7 to 28 days.

Figure 3-3-23. The FTIR spectra of 2% DMBC-treated wood sections (50 μm) before and after natural exposure for 7 to 28 days.
Figure 3-3-24. The FTIR spectra of 0.25% ACQ-treated wood sections (50 μm) before and after natural exposure for 7 to 28 days.

Figure 3-3-25. The FTIR spectra of 2% ACQ-treated wood sections (50 μm) before and after natural exposure for 7 to 28 days.
Figure 3.3.27. The FTIR spectra of 2% CCA-treated wood sections (50 μm) before and after naturally exposed for 7 to 28 days.

Figure 3.3.26. The FTIR spectra of 0.25% CCA-treated wood sections (50 μm) before and after natural exposure for 7 to 28 days.
Figure 3-3-28. The FTIR spectra of untreated control treated wood sections (50 µm) after natural exposure for 7 days.

Figure 3-3-29. The FTIR spectra of untreated control treated wood sections (50 µm) after natural exposure for 28 days.
From the overview of the FTIR spectra, the preservative treatments as well as their retention apparently influenced the photodegradation of wood mainly via delignification and demethoxylation. The photodegradation of wood was obviously accelerated by the 2.5% DDAC treatment but not by the 0.25% DDAC treatment. The treatment of 2% ACQ provided the best protection. This was followed by the 2% CCA, then 0.25% ACQ, and finally 0.25% CCA. The 2% DMBC treatment didn’t seem to enhance wood photodegradation. The relationship of wood photodegradation, preservative treatments, retention, and weathering time can be further determined by the quantitative analysis of the FTIR spectra.

Quantitative analysis of FTIR spectra

The analysis applying the internal standards, was limited, as all the absorption peaks in wood changed during weathering. The IR peak baselines were established by assuming that the baseline at 1850 cm\(^{-1}\) was zero (Mitchell et. al., 1989 and LecLerc, 1993). This method might introduce errors due to sample heterogeneity and variation in preparation. The change in absorbance at each peak was calculated from the difference in absorbance of weathered (\(A_i\)) and unweathered (\(A_o\)) samples divided by \(A_o\).

Delignification Figure 3-3-30 (a-d) shows the changes of absorbance, of the lignin peak at 1510 cm\(^{-1}\), of DDAC, DMBC, ACQ, and CCA treated, and untreated wood with weathering. For DDAC and DMBC treated and untreated samples, the delignification at 1510 cm\(^{-1}\), increased rapidly during the first 7 days of weathering, and thereafter more
gradually until the 21 days of exposure (Figures 3-3-30a and 3-3-30b). The delignification was obviously promoted by the ≥ 1% DDAC treatments, with the changes becoming obvious after the 7 and 14 days of weathering. This confirmed the previous observation that DDAC accelerated the photodegradation of lignin during weathering and that the acceleration was intensified by increasing the DDAC retention (Figure 3-3-30a). A maximum difference of a 30% occurred between the delignification of DDAC-treated sample and untreated control by 14 days exposure. This difference became smaller with longer exposure time, during which most of lignin had been removed. The demethoxylation of DDAC-treated wood and untreated controls was not quantitatively evaluated as the peak at 1267 cm⁻¹ disappeared during the early stages of the weathering process.

Delignification in ACQ and CCA-treated wood was not very extensive, although the intensity of the peak at 1510 cm⁻¹ decreased. Figures 3-3-30c and 3-3-30d showed that the delignification mainly occurred during the first 14 days of exposure and slowed down with longer exposure. The relative demethoxylation of all the ACQ-treated and CCA-treated wood gradually increased with weathering (Figure 3-3-31a and 3-3-31b). Obviously, the delignification and demethoxylation occurred via different processes. However, the trends in delignification and demethoxylation of wood for the CCA and ACQ treatments were similar. For both CCA and ACQ treatment, increasing retention provided greater protection. The comparison of ACQ and CCA treatments indicated that ACQ provided better protection against wood delignification (Figure 3-3-32a) and
Figure 3-3-30. The relative delignification (peak at 1510 cm$^{-1}$) rate of wood with natural exposure: a) untreated control and DDAC-treated, b) DMBC-treated, c) ACQ-treated and d) CCA-treated.
Figure 3-3-31. The relative demethoxylation (peak at 1267 cm\(^{-1}\)) rate of wood with natural exposure: a) ACQ-treated and b) CCA-treated.
Figure 3-3-32. The relationship between ACQ and CCA treatment and the rate of a) delignification and b) demethoxylation.
demethoxylation (Figure 3-3-32b) during weathering. The light resistance of ACQ-
treated wood may be also related to the fixation mechanism of the copper (II). As
shown in Figure 3-3-32a the relative delignification and demethoxylation demonstrated a
close relationship to the copper content. Wood treated with 1% ACQ degraded at a
similar extent to that treated with 2% CCA. Even though the copper content in the 1%
was greater than that in the 2% CCA. The later treatment also contains chromium, which
wood photodegradation.

Formation of carbonyls

Figures 3-3-33 (a-d) provides a clear picture how the
preservative and retention influenced carbonyl formation in weathered wood. For all the
samples, except those treated with 2% ACQ, the absorbance at 1720-1740 cm⁻¹ became
very intense after 7 days of exposure, and slowly increased with longer exposure periods.
Carbonyl formation in DDAC treated samples and controls (Figure 3-3-33a) was
significantly different, and much greater than that in CCA and ACQ treated wood.
Considering each treatment, the carbonyl formation varied slightly with the changes in the
DDAC or CCA retention, and markedly with change in the ACQ retention. This
observation confirmed that DDAC accelerated wood photodegradation mainly via
delignification. It also suggested that the pathway by which ACQ protects wood from
photodegradation probably differed from that for CCA. ACQ treatment provided
protection against both delignification and carbonyl formation, while CCA treatment only
prevented delignification. This observation suggested that better protection from wood
photodegradation might be attributed to the inhibition of both delignification and
Figure 3-3-33. The changes of absorbance at 1730 cm\(^{-1}\) in wood with natural exposure: a) untreated control and DDAC-treated, b) DMBC-treated, c) ACQ-treated and d) CCA-treated.
carbonyl formation. The formation of carbonyls in treated wood samples decreased in the order of DDAC > DMBC > CCA > ACQ. Since the delignification and carbonyl formation showed similar trends, the carbonyl formation might also reflect the extent of wood photodegradation.

Table 3-3-4. The Shift of Carbonyl Peaks at 1720-40 cm\(^{-1}\).

<table>
<thead>
<tr>
<th>Sample treatment</th>
<th>The wave number of carbonyl absorption peaks (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0-day</td>
</tr>
<tr>
<td>0.25% DDAC</td>
<td>1734, 1728</td>
</tr>
<tr>
<td>1% DDAC</td>
<td>1734, 1718</td>
</tr>
<tr>
<td>2.5% DDAC</td>
<td>1734, 1726, 1718</td>
</tr>
<tr>
<td>Control</td>
<td>1732, 1721</td>
</tr>
<tr>
<td>2% DMBC</td>
<td>1736</td>
</tr>
<tr>
<td>0.25% CCA</td>
<td>1734</td>
</tr>
<tr>
<td>1% CCA</td>
<td>1734</td>
</tr>
<tr>
<td>2% CCA</td>
<td>1734</td>
</tr>
<tr>
<td>0.25% ACQ</td>
<td>1736</td>
</tr>
<tr>
<td>2% ACQ</td>
<td>1734</td>
</tr>
</tbody>
</table>
Table 3-3-4 shows that carbonyl formation in the samples for the different treatments may occur via a different path, as there was no the same pattern in the shift of the peak at 1720-40 cm$^{-1}$ in the FTIR spectra of DDAC, DMBC, CCA, and ACQ treated, and untreated wood.

**Degradation of cellulose** Compared to the delignification and carbonyl formation results, the degradation of cellulose in all of the samples was minor. Figures 3-3-34a and 3-3-34b show that the cellulose degradation of the control, DDAC- and DMBC-treated wood samples increased steadily during weathering, based on the intensity of the peak at 1162 cm$^{-1}$. There was not much difference in the change of absorbance between the control, DDAC, and DMBC treatments. A greater decrease in absorbance of the cellulose peak at 1162 cm$^{-1}$ occurred in the 2% and 2.5% DDAC-treated samples than in controls after being weathered for 35 days. With the exception of the treatments at the lowest concentration (0.25%), both ACQ and CCA treatments provided good protection against cellulose photodegradation, with the amount of degradation generally remaining below 10% after 35 days weathering (Figures 3-3-34c and 3-3-34d). Both ACQ and CCA treatments demonstrated the same ability to control cellulose degradation. Figure 3-3-34a shows that the cellulose degraded faster in the last two periods of exposure, whereas lignin degraded more rapidly during the first week of exposure. The degradation pattern of cellulose agrees with Hon's suggestion (1991a) that the presence of lignin protects cellulose from photodegradation. After lignin had been removed, the cellulose was more susceptible to photodegradation.
Figure 3-3-34. The relative cellulose (peak at 1162 cm\(^{-1}\)) degradation rate of wood with natural exposure: a) untreated control and DDAC-treated, b) DMBC-treated, c) ACQ-treated and d) CCA-treated.
The observations from the analysis of the FTIR spectra showed a clear picture how DDAC and ACQ affect the delignification, carbonyl formation, and cellulose degradation during wood photodegradation. The results are in agreement with those obtained from the previous natural weathering study, and confirmed that the DDAC treatment accelerated delignification while ACQ slowed carbonyl formation and delignification. Those effects were enhanced by higher preservative retentions. The effect of DDAC on the degradation of cellulose became noticeable after lignin was degraded.

**UV-Vis reflectance spectroscopic results**

The color changes can be reflected from the increase in the absorbance with weathering over the region of wavelength longer than 400 nm as shown in the UV-Vis reflectance spectra (Figures 3-3-35, 36, 37 and 38). Figure 3-3-39 shows that the substantial changes in the spectra of 2% CCA-treated wood during the 28 days of exposure were twice those recorded for 2% ACQ-treated wood. The changes in the UV-Vis absorbance of DDAC-treated wood are greater than that in controls. Based on the UV-Vis reflectance spectra, it may be concluded that ACQ provided better control of change in wood color. These observations are in agreement with the FTIR results. The UV-Vis reflectance spectra also confirmed the visual observations that all the treated and untreated wood samples (except 2% ACQ-treated) yellowed by 14 days of exposure to weather, after which further changes at 21 days of exposure took place slowly. The change of color in the DDAC-treated and untreated samples from this experiment were
Figure 3-3-35. UV-Vis reflectance spectra of untreated wood block after natural exposure for 7 to 28 days.

Figure 3-3-36. UV-Vis reflectance spectra of 2.5% DDAC-treated wood block before and after natural exposure for 7 to 28 days.
Figure 3-3-37. UV-Vis reflectance spectra of 2% ACQ-treated wood block before and after natural exposure for 7 to 28 days.

Figure 3-3-38. UV-Vis reflectance spectra of 2% CCA-treated wood block before and after natural exposure for 7 to 28 days.
consistent with that from the previous one. In the previous experiments, we found that the weathering of DDAC-treated and untreated wood occurred at different rates. After 35 days of natural weathering, the DDAC treatment led to whitening of wood while the untreated wood become yellow. The color of 2% ACQ treated wood became lighter during the first 7 days weathering.

**Weight loss**

The weight loss for the wood samples, after exposure to weathering for 35 days, and washed with distilled water and 1% NaOH, is shown in Figure 3-3-40. The weight loss of water washed weathered wood samples ranged from 32.5% for 2.5% DDAC treated wood to 17% for 2% ACQ treated wood. The weight loss following washing with 1% NaOH was as high as 75% for 2.5% DDAC-treated wood. The wood sections treated with 2.5% DDAC, showed the highest weight loss, while the 2% ACQ-treated wood showed the least weight loss. This observation is in agreement with the FTIR analysis described earlier. With the exception of the 2% ACQ treated samples, the coloured material in all of the treated and untreated samples after weathered for 35 days dissolved immediately in 1% NaOH solution. The coloured material in the ACQ samples only partially dissolved. The degraded wood components resulting from natural exposure for 35 days were readily dissolved in 1% NaOH solution and partially in water. The extracted fraction showed a UV absorption at 280 nm. This might suggest the cleavage of lignin-carbohydrate linkage and fragmentation of lignin during weathering. The UV spectra of the water soluble component for some weathered wood sections are showed in Figure 3-
3-41. The relatively strong absorption peak at 270-280 nm indicated the presence of lignin units in the photoproducts of wood. Also, the UV absorption curves for all samples except those treated with ACQ, were similar indicating that those samples produced similar water soluble photoproducts.
Figure 3-3-40. The weight loss of wood (naturally exposed for 35 days) after washing with a) water and b) 1% sodium hydroxide solution.
Figure 3-3-41. UV-Vis reflectance spectra of water soluble of untreated control and wood treated with 2.5% DDAC, 1% DMBC, 2% ACQ, and 2% CCA, respectively, after exposure for 21 days.
3-3-3. Effect of methylation

The quantitative analysis of FTIR spectra has been used to examine effect of methylation on the compositional changes of DDAC-treated wood. Peak areas of interest were calculated by drawing a baseline from the point of transmittance at the beginning of the peak to its end. The peak was divided into two parts, described as 1510a, (the main peak), and 1510b, a shoulder attached to the main peak (Figure 3-3-42). The change of the lignin peak at 1510 cm$^{-1}$ is shown in Figure 3-3-43. After ten hours of irradiation, the amount of delignification for DDAC-treated wood was significantly greater than that of the untreated control. The relative delignification was 0.75 in 1510a and 0.88 in 1510b for 5% DDAC-treated unmethylated wood, and it was reduced to 0.59 in 1510a and 0.69 in 1510b for 5% DDAC-treated methylated wood (Table 3-3-5). The methylation did not affect the delignification of untreated controls as both methylated and unmethylated wood degraded to a similar level. The methylation improved the photostability of

Figure 3-3-42. The diagram of the calculation of lignin peak area.
Figure 3-3-43. The changes of lignin peak in a) 1510a and b) 1510b after various periods of UV irradiation.
Table 3-3-5. The changes of lignin peak area in 1510a and 1510b with UV irradiation

<table>
<thead>
<tr>
<th>irradiation time (hour)</th>
<th>(Ao-Ai)/Ao in 1510a</th>
<th>(Ao-Ai)/Ao in 1510b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>untreated, unmethylated</td>
<td>0.00</td>
<td>0.46</td>
</tr>
<tr>
<td>untreated, methylated</td>
<td>0.00</td>
<td>0.46</td>
</tr>
<tr>
<td>2.5% DDAC, unmethylated</td>
<td>0.00</td>
<td>0.65</td>
</tr>
<tr>
<td>2.5% DDAC, methylated</td>
<td>0.00</td>
<td>0.53</td>
</tr>
<tr>
<td>5% DDAC, unmethylated</td>
<td>0.00</td>
<td>0.75</td>
</tr>
<tr>
<td>5% DDAC, methylated</td>
<td>0.00</td>
<td>0.59</td>
</tr>
</tbody>
</table>

DDAC-treated wood indicating that the DDAC fixation and delignification were related. The effect of DDAC and methylation on demethoxylation followed the same trend as that on delignification (Figure 3-3-44). By removing free phenolic and carboxylic hydrogen in wood with methylation, the pathway of DDAC fixation could be blocked. The removal of DDAC fixation sites by methylation did not improve the photostability of DDAC-treated wood to the same degree as that of the untreated control. This implied that both fixed and adsorbed DDAC were responsible for the accelerated photodegradation of wood.

The changes of peak area 1510a and 1510b in samples without DDAC were the same regardless of methylation or UV irradiation time. The presence of DDAC increased
the change of peak area 1510b compared to that of peak area 1510a, but the difference between the two areas was not influenced by methylation, though methylation did reduce the change of area 1510b in the DDAC-treated samples.

After 20 hours of UV irradiation, the peak area for 1510b in 5% DDAC-treated unmethylated wood was almost undetectable while 15% of the peak area of 1510a remained unchanged. These observations suggested that the extent of delignification accelerated by DDAC was somewhat dependent on the structure of the lignin units to which DDAC might display different affinity. As shown in Figure 3-3-45, the changes of the peak area at 1730 cm$^{-1}$ for DDAC-treated wood was reduced by methylation. The comparison of the delignification, demethoxylation and carbonyl formation of modified and unmodified wood treated with DDAC has clarified the relationship between wood photodegradation and DDAC fixation. The above results clearly demonstrate that the both fixed and adsorbed DDAC must be involved in the photodegradation of wood via delignification.
Figure 3-3-44. The changes of methoxyl peak at 1267 cm$^{-1}$ after various periods of UV irradiation.
Figure 3-3-45. The changes of carbonyl peak at 1730 cm\(^{-1}\) after various periods of UV irradiation.
Chapter 4

Studies on the photodegradation of lignin model compounds

4-1. Introduction

The field of photochemistry covers all processes which involve chemical change brought about by the reaction of visible or ultraviolet radiation and these processes generally involve the direct participation of an electronically excited state of a molecule. It is generally recognized that in order to obtain a thorough understanding of photochemistry of a given system, one must elucidate the entire "life history" of the photo-process: this includes the primary process(es) and all the secondary reactions in the system. The primary photochemical process comprises the series of events beginning with the absorption of a photon by a molecule. In the primary photochemical process there is usually a variety of paths for degradation of the electronic energy of excitation. Chemical paths include intramolecular rearrangement of the formation of free radicals and excited molecules which may react in secondary processes to form new products of chemical interest. Generally, a photochemist has to be more concerned with the overall chemical changes produced by radiation and to deduce from these the nature of the primary processes involved.

The results of the previous photodegradation investigation of DDAC-treated wood showed that the treatment impacted on wood photodegradation mainly via delignification and demethoxylation. Therefore, lignin is considered to be the target where the chemistry behind this effect of the DDAC treatment, lies. Researchers have successfully used the basic lignin units with at least one of the important functional
groups (see Table 2-1-1) to imitate the photoreaction of wood. They have tended to understand the photochemistry of lignin involved in wood weathering using monomeric and dimmeric lignin model compounds (LMCs) in a solvent system (Brunow and Sivonen, 1975; Gierer and Lin, 1968; Hon, 1982; Leary, 1972; Lin and Kringstad, 1970a and 1970b; Gellerstedt and Peterson, 1977; Forsskahl, 1984a and 1984b; Castellan et al., 1987; 1988; and 1989), and in a solid carbohydrate matrix (Castellan et al., 1988; 1990; 1992 and 1993). The functional groups of lignin responsible for the photodegradation process have been identified. The carbonyl chromophore was shown to be one of the most effective reaction centers (Lin and Kringstad, 1970b; and Forsskahl, 1984a). Free phenolic hydroxyl groups are the major source of hydrogen to be donated for the hydrogen abstraction reaction, and they are further oxidized in the presence of molecular oxygen (Lin and Kringstad, 1970 and 1971; Gellerstedt and Peterson, 1977; and Forsskahl, 1984a). Excited singlet oxygen is a highly diffusible oxidizing agent which is a major factor affecting the lignin photodegradation process in solid (Gellerstedt and Pettersson, 1975). Pan and coworkers (1992) found no cleavage of lignin β-O-4 phenyl ethers during 40-50% loss of brightness in thermomechanical pulp (TMP). Most β-O-4 phenyl ethers in yellowed TMP didn’t disappear until well after the free phenols in wood have been photo-oxidized. Our previous studies showed that the acceleration of delignification by DDAC during wood photodegradation mainly occurred during the early stages of exposure to sunlight or UV radiation. It has also been found that the fixation of DDAC onto free lignin phenols was a factor affecting wood photodegradation. Those findings may imply a possible effect of DDAC on the photodegradation of lignin phenols. There is no information on the photodegradation of
lignin model compounds in the presence of AAC compounds, though the photochemistry of lignin is reasonably well understood.

In order to evaluate the effect of DDAC treatment on wood photodegradation and to build a better understanding of the photodegradation mechanisms, a series of studies have been carried out using mainly lignin model compounds and DDAC. A preliminary study investigated how DDAC and ACQ influenced the photodegradation of LMCs vanillin and guaiacol (monomeric phenols) in solution. An attempt was also made to examine the photostability of DDAC and to determine whether the presence of LMC and tertiary amine influences the photolysis of DDAC in solution. Since major bonding between DDAC and lignin were formed by ion-pairing and ion exchange (Doyle, 1995), the preferential fixation of DDAC in lignin may result in the differentiation of the photochemical and photophysical behavior of lignin units with different functional groups. The effect of DDAC on the photodegradation rate of lignin model compounds has been further investigated using six selected lignin model compounds with different kinds of functional groups in liquid phase.
4-2. Methodology

4-2-1. Vanillin and guaiacol in solution

Chemicals

Vanillin was purchased from Aldrich Chemical Inc. while guaiacol was obtained from BDH. Both chemicals were analytical grade. DDAC, ACQ, cupric acetate, and ammonia water solution were used as additives in this study. DDAC was a commercial grade Bardac® 2280 manufactured by Lonza Inc. Bardac® 2280 contained 80% DDAC active ingredient, 10% ethanol and 10% water. DMBC (Arquad® DMBC-80) was from AKZO Chemicals Inc. A stock solution of 5% ACQ (ammonia:CuO:DDAC:CO₂ = 4:2:1:1.6) prepared in the laboratory was used. Ammonium hydroxide was reagent grade, purchased from FisherScientific. An analytical grade cupric acetate was purchased from BDH. HPLC grade methanol was used for both the photoreaction and HPLC mobile phase.

Sample Preparations

Vanillin and guaiacol, were dissolved in either distilled water or a mixture of methanol and water (9:1 v/v). The solutions of DDAC, DMBC, cupric acetate and ammonia, or selected combinations of these chemicals were added to the LMC solution. The mole ratio of LMC to additive is listed in Table 4-2-1. For UV-Vis spectroscopy and HPLC measurements the concentration of aqueous vanillin solution was 1 x 10⁻⁵ g/ml while the concentration of the guaiacol methanol-water solution was 2 x 10⁻⁵ g/ml. A
portion of the solutions was used for the photoreactions, while the rest was kept in a refrigerator for subsequent HPLC analysis.

Table 4-2-1. Formulations used in the photoreaction of vanillin and guaiacol

<table>
<thead>
<tr>
<th>sample ingredient</th>
<th>mole ratio of LMC/additive</th>
</tr>
</thead>
<tbody>
<tr>
<td>vanillin only</td>
<td></td>
</tr>
<tr>
<td>vanillin, DDAC</td>
<td>1:1</td>
</tr>
<tr>
<td>vanillin, DMBC</td>
<td>1:1</td>
</tr>
<tr>
<td>vanillin, ACQ</td>
<td>1:1</td>
</tr>
<tr>
<td>methanol/water (9:1)</td>
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</tr>
<tr>
<td>guaiacol only</td>
<td></td>
</tr>
<tr>
<td>guaiacol, DDAC</td>
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</tr>
<tr>
<td>guaiacol, Cu (II)</td>
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</tr>
<tr>
<td>guaiacol, Cu (II), ammonia</td>
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<tr>
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</tr>
<tr>
<td>guaiacol, ACQ</td>
<td>1:1</td>
</tr>
</tbody>
</table>
Irradiation conditions

The LMC solutions in UV cells were sealed without degassing, and irradiated with a medium pressure quartz mercury lamp (450 watts) in a quartz cooling well, in a photoreactor chamber. The irradiation was conducted at room temperature. The flow rate of cooling water was controlled at 2.0 l/min. The samples were placed around UV lamp at a distance of 10 cm from the lamp. All the samples were stored in dark during the UV-Vis spectral measurements. At the end of irradiation, samples were kept in refrigerator for the final HPLC analysis.

Physical methods

In order to monitor the starting lignin model compound, the UV-Vis spectra of sample solutions were recorded with a Varian Cary13 UV-Vis spectrophotometer before UV irradiation and after irradiation for different periods of time. For vanillin samples, the irradiation periods ranged from 30 minutes and up to 900 minutes. The solvent was used to set the baseline for the recording of all of the spectra. A Waters HPLC system was used for the analysis of the LMCs and their byproducts. It was equipped with a 250 x 4 mm 10C18 column and a UV detector. The detection wavelength was set at 270 nanometers which was based on the observation that vanillin has a maximum UV absorption at 278 nm while that for guaiacol is at 273.5 nm. The mobile phase was a methanol/water (70/30 v/v) mixture. All samples prior to irradiation photostability of adiation and at the end of irradiation were filtered through a Teflon (PTFE) of 0.45 μm filter before being analyzed using HPLC.
4-2-2. The photolysis of DDAC

**Preparation of solid DDAC**

DDAC was extracted from the aqueous Bardac 2280 solution as follows. An aliquot of 125 ml of 5% DDAC solution was mixed with 125 ml of analytical grade methylene chloride. The DDAC-methylene chloride mixture was shaken well and then let stand for 30 minutes to allow it to separate into two layers. The methylene chloride fraction was collected while the water fraction was discarded. The methylene chloride portion was dried with sodium sulphate until the solution become clear, after which the sodium sulphate was filtered and the solvent was removed by vacuum with a Rotavapor. The solid obtained was then further dried using high vacuum, accompanied by moderate hot air heating (up to 70 °C) for four hours to remove any remaining water residue. The resulting DDAC was a cream color and powder-like solid which was stored in a desiccator over phosphorous pentoxide.

**Determination of the amount of amines in DDAC**

As the amount of amine in DDAC was not detectable using the HPLC analysis with a SCX cation ion exchange column, a titration method, adopted from AKZO Chemicals Inc., involving ion pairing precipitation was employed. The concentration of fatty quaternary ammonium salts and amines was determined by titration with a sodium tetraphenylborate solution in a hot aqueous media acidified with acetic acid. A potentiometer was used for the end point detection. During titration, the AAC forms an
ion pair with tetraphenylborate, which precipitates. A DDAC solution of 2.5% was used for titration.

**Sample preparation**

Four solutions of DDAC in ethanol-dioxane (5:1 v/v) were prepared. The formulation of each starting solution is listed in Table 4-2-2. Didecylmethylamine (DMA) and 4-O-ethyldehydrodiisoeugenol (I) were used as additives.

<table>
<thead>
<tr>
<th>sample #</th>
<th>DDAC (ppm)</th>
<th>DMA (ppm)</th>
<th>LMC I (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>250</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>250</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>250</td>
<td>0</td>
<td>125</td>
</tr>
<tr>
<td>4</td>
<td>250</td>
<td>25</td>
<td>125</td>
</tr>
</tbody>
</table>

**Irradiation conditions**

The samples (10 ml each) were placed in quartz tubes and irradiated for 13 and 26 hours with a medium pressure quartz mercury lamp (450 watts) in a quartz cooling well in a photoreactor chamber. The sample tubes were placed around the UV lamp at a distance of 10 cm from the lamp. The flow rate of cooling water was controlled at 1.7
The temperature inside the photoreactor was maintained at 27-29°C. At the end of irradiation, samples were kept in a refrigerator prior to the final HPLC analysis.

**DDAC analysis**

A Spectra Physics 1200 series HPLC system was used for the analysis of DDAC. It was equipped with a cation ion exchange Partisil SCX column of 100 x 8 mm in length by inner diameter and 10 µm in particle size and a variable wavelength UV detector. The mobile phase was a mixture of acetonitrile and water (70:30) acidified with 1.2% acetic acid and contained 0.8 g/l benzyltrimethylammonium chloride to give a positive baseline. The flow rate was 1.5 ml/min and UV-detection took place at 262 nm. The recovery of DDAC from all the reactions was determined using the peak height from the HPLC spectra.

### 4.2.3. Photoreaction of LMCs in solution

**Vanillin with DDAC added or a DDAC-tertiary amine mixture**

**Sample preparation and UV irradiation**

N, N-didecyl-N-methyl amine was provided by Lonza Inc.. Analytical grade ethanol and ethanol-water (9:1), were used for all the photo-reactions. The desired wavelength of the radiation source was achieved using Pyrex glass apparatus (λ > 300 nm). Four solutions were prepared and each solution consisted of 0.05 M (1%) vanillin, 0.0125 M (≈ 1%) DDAC, and/or 0.0125 M of DDAC and didecylmethylamine (Table 4-
2-3). The mole ratio of DDAC to DMA was 9:1. A 1 ml solution was taken from each sample and retained as stock solutions, with the rest being used for the photoreaction experiment. Two sets of samples were prepared, one at analytical scale was placed in Pyrex glass test tubes (10 ml) and the other at preparative scale was placed in Pyrex glass flasks (500 ml) and irradiated with continuous stirring in the photoreactor, at room temperature. The irradiation was maintained for up to 68 hours.

Table 4-2-3. The composition of reaction solutions

<table>
<thead>
<tr>
<th>sample #</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>composition</td>
<td>Vanillin</td>
<td>Vanillin, DDAC</td>
<td>Vanillin, DDAC, Amine</td>
<td>DDAC</td>
</tr>
</tbody>
</table>

In order to monitor the reaction progress, a predetermined amount of sample was removed from each reaction solution during irradiation for the analysis of UV-Vis spectroscopy, TLC and GC-MS. The sampling for the analytical scale experiment was done at 2, 6, 24, 36 and 68 hours of irradiation, while those at preparative scale were done at 30 and 68 hours of irradiation.
Physical methods

The UV-Vis spectra of the sample solutions were recorded with a Varian Cary 13 UV-Vis spectro-photometer.

Separation and identification of photoproducts:

After irradiation, 1 ml of solution was taken from each sample for the monitoring of the products for separation by TLC. The rest of the solution was used for the separation of photoproducts. The irradiated solution was condensed to 5 ml using a 40°C water bath with a Rotavaporator under vacuum. The white precipitate was removed by centrifuging the condensed sample, and washed three times with ethanol and then three times with acetone. The white precipitates were dried and stored for FTIR measurements, which were done using a Perkin-Elma FTIR 1600 series. The condensed samples were separated into their components using column chromatography (CC). The CC was packed with Silica gel 60 (230-400 mesh ASTM). A mixture of methanol and methylene chloride (3.5:96.5 V/V) was used as the developing agent for the TLC and the eluent solvent for the CC. Six fractions were collected from each reaction solution after CC separation. The last fraction was removed with 10% methanol in methylene chloride. The material remaining in the silica gel was extracted using ethanol-acetic acid mixture. The solvent was removed from each fraction with a Rotavaporator, and the solid obtained was stored in deep freezer prior to gas chromatography-mass spectrometry (GC-MS) analysis. A Hewlett Packard HP 5890 series II gas chromatography, equipped with VG Trio 1000 mass spectrometric detector was used. The GC column was a fused
silica capillary column (15 m long, 0.25 mm ID, 0.25 μm in film thickness) from J & W Scientific, USA.

The influence of DDAC on the photodegradation rate of LMCs

Lignin Model compounds

Six LMCs were used in this study. They were: vanillin (A), 3, 4-dimethoxybenzaldehyde (B), guaiacol (C) isoeugenol (D), 1,2-dimethoxy-4-propenylbenzene (E), and dehydrogenatediisoeugenol (F). Five of the LMCs (A, B, C, D, and E) were purchased from Aldrich, while the sixth (F) was synthesized in the laboratory. The chemical structures of those LMCs are shown in Figure 4-2-1.

![Chemical structures of Lignin model compounds](image)

Figure 4-2-1. Chemical structures of Lignin model compounds.
Synthesis and characterization of dehydrogenatediisoeugenol

Compound F was synthesized from isoeugenol according to the method of Leopold (1950). Isoeugenol 10 g (purchased from Aldrich) was dissolved in a solvent consisting of 90 ml of 95% ethanol and 40 ml of distilled water. To this solution was slowly added 14.0 g of ferric chloride in 40 ml of water while stirring the solutions. The reaction mixture was then stirred at room temperature for 2 hours, after which it was refrigerated for 20 hours. A reddish white crystalline solid was formed and collected by filtration. It was washed with 40% ethanol until the filtrate was clear. The resulting products was dried in an oven at 50°C for 4 hours. The yield was 37.7 %. The crude product was re-dissolved in methylene chloride and the solution was filtered for three times until the reddish precipitate was totally removed. In order to remove any remaining residue due to ferric compounds, the methylene solution was partitioned with water three times. The methylene chloride solution was dried with sodium sulphate anhydrite, after which it was removed by filtration. The methylene chloride solution was condensed to 30 ml using a Rotavaporator, after which hexane was added to produce a final volume of 100 ml. The resulting LMC methylene chloride-hexane solution was condensed and hexane added to the condensed solution until precipitate appeared. A white crystalline product was obtained by filtration and washing with hexane. It was identified as dehydrogenatediisoeugenol by the melting point, UV-Vis spectroscopy, FTIR, and GC-MS.

Melting point (131-132°C) was determined using the standard laboratory method, by sealing a small amount of material in a glass capillary which was then heated in oil bath. The temperature of the oil bath increased gradually at a rate of 2°C/min before
reaching melting point. The molecular weight of this compound was 326 determined by MS (m/z = 326, 100%), while the peaks in its UV spectrum (in Ethanol-water (9:1 v/v)) appeared at 204, 218, and 274 nm. The main peaks of the FTIR spectrum were at 590, 735, 757, 789, 810, 827, 862, 898, 917, 952, 1031, 1074, 1125, 1144, 1166, 1210, 1220, 1274, 1336, 1363, 1387, 1434, 1451, 1465, 1497, 1518, 1613, 2848, 2866, 2910, 2925, 2950, 3022, 3429 cm$^{-1}$.

**Sample preparation and irradiation**

Anhydrous ethanol had been used in previous experiments which showed no difference between the photodegradation rate of LMCs alone or those amended with DDAC. The higher moisture content in DDAC amended samples compared to the samples without DDAC could change the photo-activity of DDAC and LMCs. In order to avoid the interference of moisture, an ethanol-water (9:1 v/v) mixture was used as the solvent in this study. The starting concentration for all the LMC samples was 80 μg/ml. Three reaction solutions were prepared for each compound with different DDAC concentration. The ratios of LMC to DDAC were 64:0, 64:1, and 64:4 by weight. Sample irradiation was done in quartz tubes for varying periods from several minutes up to 20 minutes. None of the samples were degassed before irradiation.
**HPLC analysis**

A Waters HPLC system was used for the quantification of the starting LMCs. It was equipped with a 250 mm x 4 mm 10C₁₈ column and a UV detector. The detection wavelength was set at 270 nm which was based on the fact that all the LMCs have a maximum UV absorption around 270 nm. The mobile phase was a mixture of CH₃CN, 0.01M KH₃PO₄, and CH₃OH (40:40:20 by volume). All samples were filtered through Teflon (PTFE) 0.45 μm filter and analyzed using HPLC under prior to irradiation and at the end of each period of irradiation. The peak height was used to quantify the LMCs.
4-3. Results and discussion

4-3-1. Vanillin and guaiacol in solution

Figure 4-3-1 showed the UV-Vis spectra of vanillin in solution with and without the addition of DDAC. When the UV-Vis absorption spectra of untreated vanillin was compared to that of vanillin which contained DDAC, no differences could be observed from the spectra of the samples before and after UV irradiation. This indicated that no interaction took place between DDAC and vanillin and that the vanillin degradation was independent of DDAC under this experimental condition. Like DDAC, the addition of DMBC in vanillin also showed no effect on vanillin degradation. The HPLC analysis revealed that the amount of vanillin remaining in solutions after photodegradation for 900 minutes, was less than 5% of the starting concentration for all the samples of vanillin, vanillin-DDAC, and vanillin-DMBC. However, only a small portion of vanillin was photodegraded in the vanillin-ACQ solution. As shown in Figure 4-3-2, vanillin in the solution to which ACQ was added, slowly degraded with UV irradiation. At 780 minutes of irradiation, the UV absorption peaks of vanillin-ACQ remained strong compared to those of vanillin and vanillin-DDAC (Figure 4-3-3). This indicated that the photodegradation of vanillin was greatly inhibited by the presence of ACQ. This result is in agreement with those obtained from previous studies on the weathering of ACQ-treated wood. When ACQ was added to vanillin solution, vanillin displayed a spectrum with the usual three absorption peaks (assigned to the α-carbonyl benzene chromophore) either shifted to longer wavelength from 229 nm to 248 nm (Figure 4-3-4)
Figure 4.3.1: UV-Vis spectra of vanillin and vanillin-DDAC before and after UV irradiation.
Figure 4-3-2. UV-Vis spectra of vanillin-ACQ before and after UV irradiation.
Figure 4-3-3. UV-Vis spectra of vanillin solutions after UV irradiation for 780 minutes.

Figure 4-3-4. UV-Vis spectra of vanillin solutions before UV irradiation.
or merged from 278 and 307 nm to 346 nm. It has been reported that vanillin can react
with the copper ion II and ammonia to produce a stable complex (2vanillin-Cu(II)-2NH₃)
(Xie and Ruddick, 1995). It appeared that DDAC had no influence on the reaction
which took place between vanillin, the cupric ion, and ammonia. Vanillin could be
photostabilized in the form of such a complex (2vanillin-Cu(II)-2NH₃). The kinetics of
aromatic breakdown in vanillin are demonstrated in Figure 4-3-5. At the end of
irradiation, less than 30% of aromatics were broken down in vanillin-ACQ solution,
while more than 70% of aromatics were broken down in vanillin and vanillin-DDAC
solutions. DDAC had no significant influence on the aromatic degradation in vanillin.
In solution, the bonding between DDAC and vanillin disappeared, since both DDAC and
vanillin could move relatively freely. According to Connor and Ottewill’s theory (1971),
the bond formed by DDAC cationic ion exchange in wood may not be a true ionic bond,
but an electrostatic bond in nature. DDAC in wood could be closely associated with
lignin by either chemical bonding or physical bonding or the combination of both.
However, in solution such DDAC-lignin bonding will no longer exist. This further
supported the finding that the fixation of DDAC onto free lignin phenols was a factor
affecting wood photodegradation. Similar results were obtained from the
photodegradation of guaiacol in solutions which was monitored using UV-Vis
spectroscopic measurements and HPLC analysis. The UV-Vis spectra of guaiacol and
guaiacol-DDAC before UV irradiation were identical (Figure 4-3-6), indicating that there
was no interaction between guaiacol and DDAC. There were no significant differences
in the spectra of guaiacol and guaiacol-DDAC after UV irradiation.
Figure 4-3-5. The changes of absorbance ($A_o - A_i$)/$A_o$ at 278 nm for vanillin and vanillin-DDAC, and at 346 nm for ACQ with UV irradiation time.

Figure 4-3-6. UV-Vis spectra of a) guaiacol and b)guaiacol-DDAC in methanol, and c)guaiacol in water.
Table 4-3-1. Changes of guaiacol after UV irradiation for 2 hours, analyzed with HPLC.

<table>
<thead>
<tr>
<th>additives</th>
<th>guaiacol peak height</th>
<th>guaiacol residue (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>non-irradiated</td>
<td>irradiated</td>
</tr>
<tr>
<td>none</td>
<td>50.5</td>
<td>2.9</td>
</tr>
<tr>
<td>DDAC</td>
<td>51.5</td>
<td>—</td>
</tr>
<tr>
<td>Cu(Ac)$_2$</td>
<td>48.3</td>
<td>18.1</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>52.5</td>
<td>13.9</td>
</tr>
<tr>
<td>ACQ</td>
<td>27.2</td>
<td>12.9</td>
</tr>
<tr>
<td>Cu(Ac)$_2$ &amp; NH$_3$</td>
<td>51.5</td>
<td>26.0</td>
</tr>
</tbody>
</table>

The amount of guaiacol remaining after UV radiation for 2 hours was quantified using HPLC analysis (Table 4-3-1). The degradation rates of the guaiacol control and solution containing DDAC were not significantly different. Less than 6% guaiacol remained in both the control and DDAC contained solutions after 2 hours of UV radiation (the guaiacol peak in solution with DDAC was interfered with photoproducts), compared to 26.5%, 37.5%, 47.4%, and 50.5% of remaining guaiacol in solutions containing ammonia, Cu(AC)$_2$, ACQ, and the combination of ammonia and Cu(AC)$_2$, respectively. Copper containing chemicals and ammonia both slowed the degradation of
guaiacol. The protective effect of cupric salt was greater than that of ammonia. The combination of a cupric salt and ammonia in the form of ACQ and Cu(AC)$_2$-NH$_3$ provided the best control over the photodegradation of guaiacol with about half of the guaiacol remaining unchanged after UV radiation. This agreed with the results from the photodegradation of wood.
4-3-2. The photolysis of DDAC

When the starting concentrations of DDAC were 1000 to 1200 ppm and the samples were irradiated in quartz tubes for 3, 6, 16, and 33 hours, the photolysis of DDAC could not be detected by HPLC in any of the solutions of DDAC, DACC with a tertiary amine didecylmethylamine (DMA) 20:1 and 10:1, and those with the addition of a lignin model compound 4-O-ethyldihydrodiisoeugenol. This experiment was repeated with a lower DDAC concentration of 250 ppm, and the results of DDAC photolysis are shown in Figure 4-3-7, in which the recovery rate of DDAC was expressed as a function of irradiation time. It appeared that DDAC was very stable towards UV radiation and that the photolysis of DDAC was impeded by both lignin model compound and didecylmethylamine. Without additives, 16% of the DDAC was photolyzed during 26 hours of UV irradiation. When the lignin model compound 4-O-ethyldihydrodiisoeugenol or didecylmethylamine was introduced to the DDAC solution, photolysis reduced the DDAC content to 4 to 8%. Therefore one may conclude that the combination of 4-O-ethyldihydrodiisoeugenol and didecylmethylamine provided some protection to DDAC during 26 hours of UV photolysis. It was reported that tertiary amines may act as a photocatalyst in combination with a photosensitizer. Since the photolysis of DDAC was slowed by the presence of a LMC and amine, the lignin model compound might act as a photosensitizer to transfer energy to DDAC and/or free amines which, in turn, can catalyze the photodegradation of lignin. The photostability of DDAC under UV radiation implied that the involvement of DDAC in the photodegradation of wood would cause no structural changes to DDAC.
In order to determine how much amine is present in the extracted DDAC, solid DDAC was prepared and the amount of DDAC indirectly analyzed by titration. A DDAC solution of 2.5% was prepared and titrated. The measured DDAC concentration was found to be 2.64%. The 0.14% difference between the standard and the titration may be due to the presence of five possible amines (CH$_3$C$_{10}$H$_{21}$-NH, (C$_{10}$H$_{21}$)$_2$-NH, (CH$_3$)$_2$C$_{10}$H$_{21}$-N, CH$_3$(C$_{10}$H$_{21}$)$_2$-N). The molecular weight of these amines ranges from 157 to 311, all of which are lower than that of DDAC (362). This suggested that the extracted DDAC solid might contain at least 4.2% amines by weight.

Figure 4-3-7. The photolysis of DDAC under UV irradiation.
4-3-3. Photoreaction of LMCs in solution

*Vanillin with addition of DDAC added or a DDAC-tertiary amine mixture*

After the samples of vanillin, vanillin-DDAC, and vanillin-DDAC-didecylmethylamine (DMA) were exposed to UV irradiation screened by Pyrex glass, the colors changed from colorless to bright yellow before finally turning red brown after 68 hours of irradiation. The intensity of the red brown color decreased in the order of vanillin > vanillin-DDAC > vanillin-DDAC-DMA. A white precipitate was formed in the solution of vanillin-DDAC-DMA at 30 hours of irradiation. After 68 hours of irradiation, the amount of the precipitate formed in each solution varied from being very small for vanillin, to relatively large for vanillin-DDAC, and large for vanillin-DDAC-DMA. More precipitate was formed in the vanillin and vanillin-DDAC solutions when they were condensed from 249 ml to 4-5 ml and stored in the refrigerator for a week. The total amount of white precipitate, including those removed by centrifuging the condensed reaction solutions, represented about 5% (by weight) of the starting material for all the samples. The identical FTIR spectra of all the precipitates indicated that they were the same compound with several absorption bands similar to those of vanillin at 1675, 1588, 1505, 1456, 1422, 1400, 1355, 1311, 1279, 1258, 1182, 1149, 1079, 1044, 847, 665, 604 cm$^{-1}$ (Figure 4-3-8). The white precipitate might be a vanillin oligomer. The UV-Vis spectra of those samples showed the same trend of changes of spectra with irradiation time. Those observations implied that amine in DDAC had no detectable effect on the photodegradation of vanillin under the experimental conditions.
Figure 4.3-8. FTIR spectra of vanillin and the precipitate from the photoreaction of vanillin.
The TLC results showed that 5-6 components were presented in vanillin solution, 6-7 components in vanillin-DDAC solution, and 7 components in vanillin-DDAC-DMA solution after irradiation for 68 hours. The responses of the TLC plates indicated that some of the components were at very low concentration. Six fractions were collected from each reaction solution after CC separation. The main component of all the reactions was a vanillin residue. Four compounds have been identified in the various fractions using GC-MS. They are 4-hydroxy-3-methoxy-benzoic acid (I), 4-hydroxy-3-methoxybenzylethyl ester (II), O-decylhydroxylamine (C_{10}H_{21}-O-NH_{2}) (III), and 1-chlorodecane (IV). The MS data and GC retention time of those compounds are listed in Table 4-3-2. Compound I, caused by the photo-oxidization, was found in all the reaction solutions. Compound II, a ester of compound I and ethyl alcohol was found in the UV irradiated solutions of vanillin-DDAC and vanillin-DDAC-DMA, but not in that of vanillin. This suggested that the presence of amine or DDAC assisted the solvent effect on the formation of compound II. The chemistry behind this phenomena is not clear. Compound III was identified in the fractions of irradiated vanillin-DDAC and vanillin-DDAC-DMA solutions, but not in original DDAC. This indicated the participation of the decyl chain during the photo-reaction to produce the O-decylhydroxylamine or 1,1'-oxybisdecane compound. Compound IV was found in DDAC and a fraction from vanillin-DDAC solution after irradiation for 24 hours, but not in vanillin-DDAC and vanillin-DDAC-DMA solutions after irradiation for 68 hours. This confirmed that 1-chlorodecane disappeared with longer irradiation time. The four identified compounds were all small in quantity compared with the major fractions of vanillin and white precipitates. The results from this study might indicate that DDAC was involved in
some minor reactions during the UV exposure of vanillin in solution. This finding further confirmed that DDAC had no significant influence on the major photoreactions of vanillin in solution under the conditions of this study.

Table 4-3-2. The MS data and GC retentions of the compounds identified

<table>
<thead>
<tr>
<th>compounds</th>
<th>GC retention (min)</th>
<th>MS data (M/Z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>8.76</td>
<td>168, 153, 125, 105, 97, 91, 77, 51</td>
</tr>
<tr>
<td>II</td>
<td>9.52</td>
<td>196, 151, 137</td>
</tr>
<tr>
<td>III</td>
<td>12.92</td>
<td>171, 140, 112, 97, 85, 71, 57</td>
</tr>
<tr>
<td>IV</td>
<td>6.66</td>
<td>121, 105, 91, 85, 69, 57</td>
</tr>
</tbody>
</table>

The influence of DDAC on the photodegradation rate of LMCs

Figures 4-3-9A, B, C, D, E and F show the photodegradation rates of six lignin model compounds, vanillin (A), 3, 4-dimethoxybenzaldehyde (B), guaiacol (C), isoeugenol (D), 1,2-dimethoxy-4-propenylbenzene (E), and dehydrogenatediisoeugenol (F), in solution with and without the presence of DDAC, respectively. As shown in Figure 4-3-9A, compound A was rapidly photolyzed by UV irradiation. At 10 minutes
of irradiation, the amount of compound A remaining was 40% in the solution containing only compound A, and 50% in the solutions containing both compound A and DDAC. The presence of DDAC slowed the degradation of compound A by 10% with 10 minutes of irradiation regardless of the ratio of compound A to DDAC (line b and line c in Figure 4-3-9A). When UV irradiation continued to 20 minutes, the remaining compound A in all of the three solutions fell in the range of 2-4%. The photodegradation of compound B showed similar results with respect to the effect of DDAC (Figure 4-3-9B), as did that of compound C. At 10 minutes of irradiation, the amount of compound B remaining was about 80% in all the solutions. When UV irradiation continued to 20 minutes, the amount of compound B remaining was 46% in solution a (compound B only), 51% in solution b (B:DDAC = 64:1), and 56% in solution c (B:DDAC = 16:1). A similar trend was observed in the degradation of compound C as well (Figure 4-3-9C) with 59% of compound C remaining in solution a compared to 72% in solution c after the samples were exposed to UV irradiation for 10 minutes. The difference between the degradation rates of compound C in solution a and solution c increased to 20% at 20 minutes of UV irradiation. The slower degradation rates of compounds A, B and C in the presence of DDAC indicated an inhabiting effect of DDAC on the photodegradation of the three compounds under the conditions of this experiment. The degradation of compounds A, B, and C was slowed slightly by increasing the DDAC concentration.

As shown in Figures 4-3-9D, E, and F, the photodegradation rates of each of these LMCs in solution, with and without DDAC, were all similar. The observations suggested that DDAC had no apparent effect on photodegradation of these compounds.
It was obvious that the observations from the compounds A, B and C were different from those recorded for the compounds D, E and F. The differences might result from the photoreactivity of the two sets of compounds containing different functional groups. Compounds D, E and F all contain an \( \alpha \) C=C group while compounds A and B contain an \( \alpha \) C=O group and compound C contains neither \( \alpha \) C=C nor \( \alpha \) C=O group. Based on the photodegradation rate, the compounds with \( \alpha \) C=O group were more likely affected by the presence of DDAC than compounds with \( \alpha \) C=C group. One of the possible explanation for this difference might be that the photo-energy absorbed by compounds A, B and C was more prone to being transferred to DDAC which in turn deactivated the excited molecule. Consequently, the photoreaction of this excited molecule would be terminated. The energy transfer from an excited molecule to DDAC actually protected this molecule from decomposition or conversion. The catalytic effect of DDAC in wood might not be applicable in solution due to the lack of chemical interaction between DDAC and lignin model compounds, solvent effects and other differences between solid and solution, such as, free radical mobility. Rabek (1987) has emphasized that due to the restricted mobility of polymer chain, it maybe difficult to transfer kinetic results collected from measurements in solution to solid polymers. Hon (1992) has noted that the solvent effect on energy transfer as well as its participation in the photochemical reactions were not considered in the photodegradation of wood. Consequently, the photochemical reactions of solid lignin may differ considerably from those lignin model compounds in solution (Hon, 1992).
The photo-reactivities of the six model compounds were, in the decreasing order \( F < A < C < B < E < D \), as displayed in Figure 4-3-10. Compounds D and E with an \( \alpha \) \( C=C \) group were more reactive than those A and B with an \( \alpha \) \( C=O \). When the phenolic compounds A and D were methylated, the photo-reactivities of their derivatives (B and E) decreased. Compound F, derivatized from D, displayed a reduced photoreactivity, and was more stable than compounds D and E towards photodegradation.

As shown in Figures 4-3-9A, B, D and E, the extent of the effect of DDAC on the photodegradation of lignin model compounds was independent of the presence of a free phenolic hydroxyl group in them, though it did vary when the functional groups \( \alpha \) \( C=C \) or \( \alpha \) \( C=O \) were present. Compounds B and E were derivatized from compounds A and D by methylation, in which the phenolic hydroxyl group was replaced by a methoxyl group. Following photoexposure, when 37% of compound A and 46% of compound B remained in solutions containing no DDAC, 49% of compound A and 56% of compound B remained in the solutions containing DDAC (LMC:DDAC = 16:1) (Figure 4-3-11). The comparison of these degradation rates suggested that little or no interaction took place between the phenolic hydroxyl group and DDAC in solution. A similar result was obtained from compound D and E. This further confirmed that the lack of a significant DDAC lignin interaction might be the most likely explanations for the results from solution and the previous studies on the photodegradation of wood.

From the results obtained on the photoreaction of LMCs in solution, it was concluded that the studies involving the solutions of LMCs do not reflect the photoreaction processes which occur at the surface of wood during weathering. Since the
results from studies with LMCs contrasted with those from wood where the essential role of DDAC fixation to wood photodegradation was clearly apparent, the appropriateness of studying LMC reactions in solution to examine the mechanisms by which DDAC influences the weathering of treated wood is therefore limited.
Figures 4-3-9A-F. The photodegradation of LMCs-A, B, C, D, E, and F with the ratio of LMC to DDAC (by weight): a, LMC only; b, 64:1; c, 16:1

Figure 4-3-9A. The photodegradation of compound A.

Figure 4-3-9B. The photodegradation of compound B.
Figure 4-3-9C, The photodegradation of compound C.

Figure 4-3-9D, The photodegradation of compound D.
Figure 4-3-9E. The photodegradation of compound E.

Figure 4-3-9F. The photodegradation of compound F.
Figure 4-3-10. The photodegradation of LMCs-A, B, C, D, E, and F.

Figure 4-3-11. The photodegradation of compounds A and B.
Chapter 5

Studies on free radicals in wood

5-1. Introduction

One of the most remarkable features of ESR spectroscopy is its high sensitivity for detecting elements having unpaired electrons present in a sample. The formation, behavior, and type of free radicals as intermediates of a photo-reaction can be determined by the intensity of free radical signals and g values calculated from the ESR spectra. As mentioned in the literature review, photodegradation of wood surface has been known to occur via numerous free radical chain reactions. Several types of free radicals, such as phenoxy, alkoxy and carbon radicals, with different reactivities that are distributed on the photo-irradiated wood surfaces have been recognized using ESR technique (Hon, 1991). However, there is no information available regarding the characteristics of free radicals generated during the photodegradation of DDAC-treated wood. How does DDAC affect the free radical formation and behavior? It has been suggested that quats can initiate the polymerization of some alkene monomers in bulk or in solution (Otsu et. al., 1969; Ko et. al., 1974; Ratcliff and Kochi, 1971; Kita et. al., 1980; Pac and Kakurai, 1968; and 1969). However, it is not clear whether this process can occur during the photodegradation of DDAC-treated wood. In order to answer those questions, the formation and decay of free radicals in treated and untreated wood during UV irradiation was examined using ESR spectroscopy. This study attempted to establish whether the free radical formation and decay of wood was related to DDAC treatment, chemical retention, and fixation and the effect of DDAC treatment on wood photodegradation.
The ESR spectroscopy of free electrons is based on the paramagnetism of free electron spins, for this reason one also speaks of electron paramagnetic resonance (EPR). Electrons in fully occupied molecular orbitals generally do not give rise to a magnetic moment since - according to the Pauli principle - pairwise spins compensate each other. But, a free radical is not paired, and hence the effect of its spin is not canceled. The energy states of electron spin separate in an applied magnetic field (Figure 5-1-1). Resonance occurs when the frequency of incident microwave radiation matches the frequency (ν) corresponding to the energy separation (hv) which depends on the strength of the magnetic field (B):

\[ hv = g_e \mu_B B \]

where \( g_e \) is the spectroscopic splitting factor (also called G value), and \( \mu_B \) is the electron Bohr magneton.

![Diagram of electron spin levels in an applied magnetic field](image)

Figure 5-1-1. The electron spin levels in an applied magnetic field.
At resonance, strong absorption of the radiation occurs which is referred to as the ESR signal. The ESR signal depends upon the orientation of the spin of an unpaired electron in a changing external magnetic field. This property permits the detection not only of stable free radicals but of short-lived radical intermediates in chemical reactions and can even give information about their structure.

Generally, the incident radiation frequency employed by commercially available ESR spectrometers is fixed (at about 9.5 GHz) and the magnetic field is swept through a range of values above and below optimum conditions for resonance.
5-2. Methodology

Preparation of ESR samples

Air-dried southern yellow pine sapwood was used in this study. The moisture content was about 4.5% determined on an oven-dried weight. The earlywood strips were cut from a block with the dimensions of 25 mm (tangential) x 20 mm (radial) x 35 mm (longitudinal), and the samples typically contained 4 annual rings. For each treatment condition, ten cylindrical shaped match sticks weighing around 30 mg each were prepared from the same annual ring of an air-dried wood strip. Five sticks were used for the examination of the effects of a chemical treatment while the other five match sticks were retained as untreated controls for comparison with the treated samples.

The treatment of the match sticks was carried out using vacuum impregnation with either the aqueous preservative solution or distilled water for untreated controls. The excess liquid on the sample surface was removed with Kimwipes® tissue. After treatment, each of the match sticks was weighed and sheltered from light in open air for air drying. Table 5-2-1 shows the weight of the wood sticks, and preservative uptake.

DDAC, DMBC, and ferric chloride were used as treating chemicals in this study. As described in the section 3-2-1, the aqueous DDAC solutions of 1%, 2.5%, and 5%, were prepared from a commercial grade Bardac® 2280, and aqueous DMBC solution of 2.5% were prepared from Arquad® DMBC-80 provided by AKZO Chemicals Inc. The DDAC and DMBC solutions were done using distilled water to dilute the concentrated solutions.
Table 5-2-1. The preservative uptake of wood treated with aqueous DDAC solution

<table>
<thead>
<tr>
<th>Wood Sticks</th>
<th>Weight (mg)</th>
<th>Uptake (DDAC/wood by wt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial Wt. (air-dried)</td>
<td>Wet Wt. (aft. treatment)</td>
</tr>
<tr>
<td>Treatments</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% DDAC-1</td>
<td>30.12</td>
<td>116.87</td>
</tr>
<tr>
<td>5% DDAC-2</td>
<td>31.33</td>
<td>114.76</td>
</tr>
<tr>
<td>5% DDAC-3</td>
<td>31.14</td>
<td>129.26</td>
</tr>
<tr>
<td>5% DDAC-4</td>
<td>28.19</td>
<td>117.54</td>
</tr>
<tr>
<td>5% DDAC-5</td>
<td>35.38</td>
<td>124.10</td>
</tr>
<tr>
<td>2.5% DDAC-1</td>
<td>35.2</td>
<td>119.4</td>
</tr>
<tr>
<td>2.5% DDAC-2</td>
<td>35.7</td>
<td>117.2</td>
</tr>
<tr>
<td>2.5% DDAC-3</td>
<td>37.8</td>
<td>126.4</td>
</tr>
<tr>
<td>2.5% DDAC-4</td>
<td>35.4</td>
<td>116.4</td>
</tr>
<tr>
<td>2.5% DDAC-5</td>
<td>35.3</td>
<td>120.1</td>
</tr>
<tr>
<td>1% DDAC-1</td>
<td>33.5</td>
<td>120.4</td>
</tr>
<tr>
<td>1% DDAC-2</td>
<td>31.8</td>
<td>113.9</td>
</tr>
<tr>
<td>1% DDAC-3</td>
<td>29.4</td>
<td>108.2</td>
</tr>
<tr>
<td>1% DDAC-4</td>
<td>28.5</td>
<td>105.2</td>
</tr>
<tr>
<td>1% DDAC-5</td>
<td>27.0</td>
<td>99.7</td>
</tr>
</tbody>
</table>
chemicals. The FeCl₃ water solution (10 mmol/l) was prepared with a analytical reagent FeCl₃ supplied by Baker.

**Leaching**

2.5% DDAC treated wood sticks were immersed in distilled water, subjected to vacuum impregnation and pumping for 30 minutes and then placed in an ultrasonic bath for 2 hours. They were removed from the ultrasonic bath, washed three times with fresh distilled water and air-dried in the dark.

**UV irradiation and ESR measurements**

The ESR sample was inserted into a suprasil™ quartz tube which was then sealed with rubber tubing under atmospheric conditions. The tube (with sample) was first frozen for at least 15 minutes in liquid nitrogen prior to UV irradiation after which it was inserted into a finger Dewar flask filled with liquid nitrogen. The finger tip of the Dewar was made of clear quartz which allowed UV light to pass through. The UV irradiation of ESR samples was done outside the ESR cavity at liquid nitrogen temperature. The finger Dewar flask was placed in a photo-reactor equipped with a medium pressure mercury lamp. The distance between UV source and sample tube was 15 cm. The irradiation time varied from 8 minutes up to 72 minutes.

Before irradiating samples, the ESR spectra of two empty quartz tubes were recorded at 150 °K. Both tubes were irradiated for 5 and 15 minutes. The ESR signals of the empty tubes, produced by UV irradiation, were centered at 3160 G, which will not interfere with the major free radical signal in wood. The ESR spectra of wood sticks were
recorded under the conditions of a) before UV irradiation, b) after different periods of irradiation, and c) after allowing the samples to warm up for 5 minutes up to 15 minutes.

A Brucker ECS 106 ESR spectrometer was used to record the spectra of wood samples under various conditions. All of the ESR measurements were carried out at 150 °K by transferring the ESR sample tube from the Dewar flask to the ESR cavity. The parameters of this instrument are listed in Table 5-2-2.

Table 5-2-2, The parameters of the ESR spectrometer

<table>
<thead>
<tr>
<th>General</th>
<th>detection temperature</th>
<th>150 °K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>number of scans</td>
<td>8</td>
</tr>
<tr>
<td>Receiver</td>
<td>modulation frequency</td>
<td>50 kHz</td>
</tr>
<tr>
<td></td>
<td>modulation amplitude</td>
<td>0.642 G</td>
</tr>
<tr>
<td></td>
<td>receiver gain</td>
<td>1.00e + 04</td>
</tr>
<tr>
<td>Signal channel</td>
<td>conversion</td>
<td>20.48 ms</td>
</tr>
<tr>
<td></td>
<td>time constant</td>
<td>5.12 ms</td>
</tr>
<tr>
<td></td>
<td>sweep time</td>
<td>83.886 s</td>
</tr>
<tr>
<td>Field</td>
<td>center field</td>
<td>3414.00 G</td>
</tr>
<tr>
<td></td>
<td>sweep with</td>
<td>1000.00 G</td>
</tr>
<tr>
<td></td>
<td>resolution</td>
<td>4096 points</td>
</tr>
<tr>
<td>Microwave</td>
<td>power</td>
<td>10 mw</td>
</tr>
<tr>
<td></td>
<td>frequency</td>
<td>9.57 GHz</td>
</tr>
</tbody>
</table>
5-3. Results and discussion

All the ESR spectra of wood samples were recorded at 150 °K. This detection temperature was chosen based upon the limitations of the instrument and the fact that information available in the literature suggested that detection of short lived free radicals in wood can be conducted successfully at this temperature. Hama and Shinohara (1970) found that the relative signal intensity of ESR spectrum of polycarbonate began to decrease at temperatures higher than 203 °K (Figure 5-3-1). The polycarbonate was ultraviolet-irradiated at 77 °K for 60 minutes. Initial experiments in the present studies confirmed that the intensity of free radicals after being UV-irradiated for short periods did not change significantly when detection temperatures were varied from 120 °K to 170 °K.

![Figure 5-3-1. Relationship between relative intensity (R.I.) and temperature (°K) of heat treatment for polycarbonate UV-irradiated at 77°K (Hama and Shinohara, 1970).](image)
**DDAC Treatment**

Figures 5-3-2 and 5-3-3 show the ESR spectra of untreated and DDAC treated match sticks respectively, after different periods of UV-irradiation. All the samples yielded easily detectable ESR signals. A singlet ESR peak centered at 3414 G with a g value of 2.0046 was present in all the wood samples. The shape of the ESR spectrum for the DDAC-treated wood and untreated control were very similar. With longer UV irradiation times, the spectra appeared to be broadened. After 16 minutes of irradiation, the line width between the points of maximum slope were 40 gausses for the untreated control and 45 gausses for the 5% DDAC-treated wood. Figure 5-3-4 shows the relative intensities (peak to peak distance) of ESR signals of 1%, 2.5% and 5% DDAC-treated, 2.5% DMBC treated, and untreated samples with respect to irradiation time. The initial free radical intensity for all the treated samples was lower than those of untreated sample. This implied that there were fewer stable free radicals present on the surface of treated wood before exposure to UV irradiation.

During UV irradiation, the free radical concentration gradually increased for all of the untreated samples with a relatively rapid increase during the first period (8 minutes) of irradiation, and a smooth increase in the second and third periods. Following these first three periods, the free radical intensity remained almost constant with longer irradiation (Figure 5-3-4). This suggested that the initiation of photodegradation at the wood surface occurs during the first 8 to 16 minutes of UV irradiation under the conditions of this experiment. A very obvious phenomenon, appearing in all the DDAC-treated samples, was the sharp increase in free radical formation due to the effect of DDAC sensitization.
Figure 5-3-2. ESR spectra of untreated wood after UV irradiation for different periods.

Figure 5-3-3. ESR spectra of DDAC-treated wood after UV irradiation for different periods.
Figure 5-3-4. The free radical intensity of untreated controls and DDAC and DMBC-treated and wood.

a. 1% DDAC

b. 2.5% DDAC
Figure 5-3-4. The free radical intensity of untreated controls and DDAC and DMBC-treated and wood. (continued)
The higher the DDAC retention, the earlier the sensitization appeared (Figures 5-3-4 a, b, c, d). For the 1% DDAC-treated wood sensitization appeared at the 32 minutes of irradiation, at the 16 minutes UV exposure for 2.5% DDAC-treated wood, and at 8 to 16 minutes for 5% DDAC-treated wood. In addition, the relative signal intensity also increased with increasing DDAC retention (Figures 5-3-5 a, b, c). This phenomenon indicated that DDAC may function as either a photo-initiator or photosensitizer. From the FTIR studies described earlier (section 3-3-3), it was found that the increase in wood photodegradation produced by DDAC was greater at higher DDAC retentions. In the two separate experiments, the ESR study showed that DDAC promoted free radical formation, while the FTIR study revealed that DDAC enhanced wood photodegradation (mainly delignification). So, we can conclude that DDAC promoted free radical formation was related to the photodegradation of wood. No sensitization effect was observed for 2.5% DMBC-treated wood (Figure 5-3-4d). Compared with untreated samples, DMBC treatment did not have much influence on the free radical formation. This is also consistent with the results of FTIR studies from which it was found that DMBC did not enhance delignification during wood photodegradation.

Figure 5-3-6 shows the relative intensity of unstable free radicals following warming of the test samples. In order to determine the relative amount of stable and unstable free radicals, after ESR measurement at the end of UV-irradiation, the sample tubes were removed from the ESR cavity, warmed to room temperature for 5 and 15 minutes, and then cooled again in a Dewar flask filled with liquid nitrogen before recording the ESR spectra. At each warming stage, the amount of free radical lost represented a group of free radicals with similar stability. It is of importance to point out
Figure 5-3-5. The increase in the free radical intensity of untreated controls and DDAC and DMBC-treated and wood.

a. 1% DDAC

b. 2.5% DDAC
Figure 5-3-5. The increase in the free radical intensity of untreated controls and DDAC and DMBC-treated and wood. (continued)

c, 5% DDAC

![Graph showing the increase in free radical intensity for 5% DDAC with control and 5% DDAC lines.]

d, 2.5% DMBC

![Graph showing the increase in free radical intensity for 2.5% DMBC with control and 2.5% DMBC lines.]
Figure 5-3-6. The relative intensity of unstable free radicals at the end of UV irradiation.
that those free radicals that are detectable by ESR spectroscopy in the samples warmed to room temperature are relative stable ones. Most of short-lived free radicals are unable to survive at room temperature (Hon et. al., 1980). The relative signal intensity of unstable free radicals was calculated from the difference in the signal intensity at each warming stage and that at the end of irradiation, which represented the amount of free radicals decayed by warming. It was clear that the relative intensity of unstable free radicals in DDAC-treated samples was higher than that of untreated controls, regardless of DDAC concentration (Table 5-3-1). The unstable free radicals served as reaction sites to trigger additional free radical chain reactions (Hon, 1988). The rate of a photoreaction is mainly dominated by the reactivity of the free radicals involved. The more active free radical intermediates formed in DDAC-treated wood suggested that more rapid photoreaction occurred than in the control samples during UV-irradiation of wood.

Table 5-3-1. The ratio of unstable free radical intensity of DDAC-treated wood to untreated wood at the end of UV-irradiation.

<table>
<thead>
<tr>
<th>DDAC conc.</th>
<th>warmed for 5 min</th>
<th>warmed for 15 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%</td>
<td>1.3</td>
<td>N/A</td>
</tr>
<tr>
<td>2.5%</td>
<td>1.1</td>
<td>1.6</td>
</tr>
<tr>
<td>5%</td>
<td>1.4</td>
<td>1.2</td>
</tr>
</tbody>
</table>
Table 5-3-2 shows the relation of stable free radicals among DDAC-treated and untreated samples. Fewer stable free radicals were found in all the DDAC-treated samples, but their concentration didn't seem to be related to DDAC retention in wood. When the irradiated samples were stored in darkness for 1 to 6 days, the free radical intensity of all the samples decayed to the levels of that before irradiation. This observation demonstrated that some of the stable free radicals decayed slowly in darkness. It has been reported that a significant reduction occurred in free radical contents for lignin preparations and wood after storage in darkness (Ranby et al., 1969). Based on stability, the free radicals trapped on the wood surface under this experimental conditions might be classified into three groups: short-lived and unstable, relative stable but slowly decayed, and stable at room temperature. The comparison of free radical intensity of the three groups from DDAC-wood and untreated controls indicated

<table>
<thead>
<tr>
<th>DDAC conc. →</th>
<th>1%</th>
<th>2.5%</th>
<th>5%</th>
</tr>
</thead>
<tbody>
<tr>
<td>sample conditions ↓</td>
<td>DDAC</td>
<td>control</td>
<td>DDAC</td>
</tr>
<tr>
<td>before irradiation</td>
<td>1.5</td>
<td>4.2</td>
<td>2.0</td>
</tr>
<tr>
<td>warming for 5 min</td>
<td>6.0</td>
<td>8.5</td>
<td>6.3</td>
</tr>
<tr>
<td>warming for 15 min</td>
<td>4.2</td>
<td>7.6</td>
<td>4.7</td>
</tr>
</tbody>
</table>

Table 5-3-2, The intensity of relatively stable free radicals.
that the presence of DDAC had an influence on the formation and decay of all the free radicals, even the intrinsic ones. The intrinsic free radicals are those generated during wood preparation as well as by exposure to light and remain stable at room temperature (Hon et. al., 1980).

As mentioned earlier, DDAC treatment of wood had no influence on spectral shape and $g$ value. Based on the $g$ value (2.0046), the major component of free radicals, generated in wood during UV-irradiation likely were phenoxy radicals. Hama and Shinohara (1970) have reported that phenoxy and phenyl radials were generated from UV-irradiated polycarbonate ($(-\text{OOCO-C}_6\text{H}_4-\text{C(CH)}_2\text{-C}_6\text{H}_4-)_n$), and that the ESR spectra of polycarbonate have no appreciable hyperfine structure and consist of a singlet and having a $g$ value of 2.0045. It was demonstrated that the decay of free radicals occurred with elevation of temperature at higher than 203°K (Hama and Shinohara, 1970). In softwood lignin (milled wood lignin), three out ten $C_9$ units are of a free phenolic nature (Alder, 1977). UV irradiation would create phenoxy radials in lignin (Kringstad and Lin, 1970). On the basis of observations from this experiment and literature, it is reasonable to conclude that the free radicals were generated mainly from the lignin in wood for both DDAC-treated and untreated controls.

The stability of phenoxy radicals depends on their molecular structure. For examples, a phenoxy radical with a biphenyl structure is stable even at 25°C (Hon, 1988). Since the presence of DDAC in wood influences not only the formation of free radicals but also their decay (mainly phenoxy radicals), DDAC affecting wood photodegradation are presumably related the interaction of DDAC and lignin in wood. It remains to be
determined whether it is the fixed, adsorbed DDAC, or both that plays a major role in affecting free radical formation and decay.

**Leaching**

To examine whether the fixed DDAC has the major effect on free radical formation in wood, the physically adsorbed DDAC was removed by leaching the wood with distilled water. The air dried 2.5% DDAC-treated wood sticks were used in this study. The remaining DDAC in the leached wood was mainly fixed by ion-exchange. According to Doyle (1995), the amount of DDAC physically adsorbed in wood and lignin accounts for 87% and 74% of the total DDAC adsorbed, respectively. This portion of DDAC can be desorbed by washing with water.

Figure 5-3-7 shows the formation of free radicals in leached and unleached 2.5% DDAC-treated wood during UV irradiation. In the first 8 minutes of irradiation, the same amount of free radials were found for both of the samples. At 16 minutes, slightly more free radicals formed in the unleached sample. The DDAC sensitization occurred at 24 minutes of irradiation for unleached sample while it occurred at 48 minutes with a peak at 56 minutes of irradiation for the leached samples. The intensity of the signal peak, the spectral shape, and g value were identical for both of the samples. The above observations demonstrated that the fixed DDAC in wood played a major role in its sensitization, though the fixed DDAC by ion-exchange was about one tenth of the total DDAC. In the early section of this study, it was found that the irradiation time at which DDAC sensitization took place was dependent on the DDAC retention. Comparison of this result with the
leaching study indicated that the DDAC physically adsorbed in wood could promote the DDAC sensitization but was not essential for its occurrence.

After the DDAC sensitization, how further effect would DDAC have on free radical formation? When UV irradiation was allowed to continue after the sensitization effect, the free radical intensity based upon the ESR signal of DDAC treated samples decayed to a similar level to that of untreated ones. However, DDAC continuously and smoothly promoted the formation of free radicals with prolonged irradiation. As shown in Table 5-3-3, the trend of free radical formation with continuous UV-irradiation was expressed by the slope of the difference in free radical intensity over the irradiation time span. Compared with the untreated controls, all the DDAC treated samples showed higher slope values which increased with the greater DDAC retention, from 12.5 for 1%, 21.2 for 2.5% to 57 for 5% DDAC-treated wood. The slope was 11.2 for the unleached sample and only 3.7 for the sample that was leached. The higher slope value implies a faster growth in free radical formation. The overall impression from the slope result was that the free radical formation with the post-sensitization irradiation was related to not only the presence of DDAC but also the amount. This observation further confirmed that the DDAC physically adsorbed in wood could promote free radical formation over the post DDAC sensitization period.
Figure 5.37. The free radical intensity of 2.5% DDAC-treated wood.
Table 5-3-3, The slope of the intensity of free radical formation in wood against irradiation time in the last period of irradiation.

<table>
<thead>
<tr>
<th>DDAC treatment</th>
<th>Δintensity/min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>treated wood</td>
</tr>
<tr>
<td>5%</td>
<td>57.0</td>
</tr>
<tr>
<td>2.5%</td>
<td>21.2</td>
</tr>
<tr>
<td>1.0%</td>
<td>12.5</td>
</tr>
<tr>
<td>2.5%, unleached</td>
<td>11.2</td>
</tr>
<tr>
<td>2.5%, leached</td>
<td>3.7</td>
</tr>
<tr>
<td>2.5%, long irrdn</td>
<td>10.8</td>
</tr>
</tbody>
</table>

**FeCl₃ treatment**

FeCl₃ as a photosensitizer in the photodegradation of cellulose has been widely studied (Ogiwara and Kubota, 1973; Hon, 1975c; and Hon, 1980). Ogiwara and Kubota found that the relative signal intensities of the ferric ion sensitized cellulose after being irradiated with a high pressure mercury lamp for 60 minutes doubled that of untreated control. They also reported that the cellulose radicals produced in the presence of the photosensitizer were very unstable when the sample was warmed, and that the photoreaction resulted in a significant increase of scission of cellulose chains. Hon (1980) proposed that cellulose interacts with the ferric ion to form a cellulose-iron complex,
which is able to absorb and transfer energy to the cellulose backbone effectively, to
initiate free radical formation.

What kind of effect could ferric chloride have on the formation and decay during
wood photodegradation? The wood treated with ferric chloride has been examined using
ESR spectroscopy before and during UV irradiation. Figure 5-3-9 shows the relative
intensity of free radicals with irradiation time. The curve of free radical formation was the
same as that DDAC treated samples (Figure 5-3-5). The ferric chloride sensitization
occurred at 48 minutes of irradiation, which was similar to that of 2.5% DDAC-treated
wood leached with water. The ESR spectral shape and $g$ value of the FeCl$_3$ treated
sample, as compared to that of the DDAC-treated samples, showed no difference (Figure
5-3-10).

It has been reported that QACs function as photoinitiators producing a cation-
radical in solution and bulk systems (Otsu et. al., 1969; Ho et. al., 1974; and Ratcliff and
Kochi, 1971), although none of the cation radicals have been identified by ESR
spectroscopy. A photosensitizer is defined as a chemical compound or a chemical system
which sensitizes the photoreaction by an energy transfer mechanism and retains its
chemical structure unchanged through out the photoreaction. On the other hand, a
photoinitiator is a chemical compound or chemical system which absorbs light and
dissociates into free radicals. Under these definitions, if DDAC behaved as a
photoinitiator in the reaction, it should have been destroyed. From the study of DDAC
photolysis, it was found that DDAC in solutions was very stable towards UV irradiation.

From this study, it is proposed that DDAC functions as a photosensitizer during
the photodegradation of wood. The sensitization probably takes place via the DDAC-
lignin complex, which can promote free radical formation by energy transfer. Both of the physically adsorbed DDAC and the fixed DDAC were considered to be responsible for the formation and decay of free radicals. This may explain the previous observation that the fixed DDAC is only one of the factors affecting wood photodegradation.

Figure 5-3-8. The free radical intensity of ferric chloride-treated wood.
Figure 5-3-9. ESR spectra of wood treated with 2.5% DDAC, a) unleached and b) leached; c) 5% DDAC; and d) 10 mmol FeCl₃.
Chapter 6

Summary

The initial experiments focused on the chemical changes in DDAC- and ACQ-treated wood during treatment (fixation), weathering, or UV irradiation. An FTIR technique was developed which allowed the direct repetitive examination of a sample at the same location throughout an experiment. Interaction between DDAC and ACQ treatments and wood caused the lignin peak at 1510 cm\(^{-1}\) to split and decrease in intensity, while no changes were detected for the cellulose peaks. This was interpreted as suggesting preservative fixation primarily to lignin in wood. This conclusion was further supported by the reduction in the intensity of the lignin peak at 1425 cm\(^{-1}\) in both ACQ and DDAC-treated samples. The decrease of the phenolic hydroxyl absorption at 1645-1660 cm\(^{-1}\) following DDAC and ACQ treatment, confirmed the cation-ion exchange of the hydroxyl group with DDAC and ACQ. The carbonyl peak at 1730 cm\(^{-1}\) was unchanged in DDAC-treated wood, but decreased in ACQ-treated wood. The decreases in peak intensity at 1510 and 1730 cm\(^{-1}\) were consistent with the formation of a complex between ACQ and phenolic hydroxyl and carbonyl groups.

The effect of sample thickness on wood photodegradation was determined. The natural weathering study demonstrated that DDAC treatment accelerated the weathering of wood by enhancing delignification and demethoxylation, based on the rate of disappearance of the FTIR absorptions at 1510 and 1267 cm\(^{-1}\). The broadening and increase of the carbonyl absorption in both untreated and DDAC-treated samples, confirmed their production during weathering. ACQ slowed wood photodegradation as
demonstrated by the slow formation of carbonyl groups and delignification. After 35 days of weathering, the FTIR spectra of the ACQ samples did not show any significant changes in the intensities of the peaks at 1720-1740, 1600, 1510 and 1267 cm\(^{-1}\), suggesting that ACQ had stabilized lignin against photo-degradation. Cellulose was not affected during the weathering, based on the lack of change in the intensity of peak at 1162 cm\(^{-1}\).

The UV irradiation study showed similar FTIR spectral changes compared to those obtained from natural weathering. Delignification in UV irradiated wood decreased in the sequence of DDAC > control >> ACQ. As found for the natural weathering, compared to lignin, cellulose was degraded to a much less extent. The photochemical reaction in the laboratory appeared to accurately reproduce the effects of natural weathering.

Quantitative analysis of artificially UV irradiated samples showed that DDAC accelerated the wood photodegradation rate via both delignification and demethoxylation. For ACQ-treated samples, demethoxylation occurred at a greater rate than delignification.

A second weathering study compared the influence of DDAC, DMBC, ACQ and CCA treatments and their retention on wood photodegradation. From the FTIR spectra, it was observed that delignification and demethoxylation were accelerated by DDAC treatment and slowed by ACQ and CCA treatments. These effects were enhanced by greater preservative retention. A maximum difference of a 30% occurred between the delignification rate of DDAC-treated samples and untreated controls after 14 days of exposure. This difference became smaller with longer exposure time, as most of the
lignin had been removed. Considering each treatment, the carbonyl formation varied only slightly with DDAC or CCA retention, but markedly with ACQ retention.

ACQ provided better protection against wood photodegradation than CCA. The light resistance of ACQ-treated wood based upon the relative delignification rate and demethoxylation rates, correlated with the fixation of the copper (II). The degradation of cellulose in all of the samples was minor, only becoming noticeable after lignin had been degraded. Compared to controls the decrease in absorbance of the cellulose peak at 1162 cm\(^{-1}\) was greater in the 2% and 2.5% DDAC-treated samples, after 35 days of weathering.

The changes at the wood surface as monitored by UV-Vis reflectance spectra were in agreement with the FTIR results. The chemical changes for all the treated and untreated samples mainly occurred during the first 7 to 14 days of weathering. The weight loss of weathered samples following leaching with water and sodium hydroxide solution confirmed the relative weathering resistance of the DDAC-, CCA- and ACQ-treated and untreated wood.

In order to clarify the relationship of the DDAC fixation and photodegradation, FTIR analysis examined how methylation effected the weathering in DDAC-treated wood. Methylation did not affect the delignification of untreated controls. However, methylation improved the photostability of DDAC-treated wood, confirming the role of "fixed" DDAC in promoting delignification. Since even with the improvement, DDAC-treated wood was photochemically less stable than the untreated controls, it can be concluded that both fixed and adsorbed DDAC accelerate photodegradation of wood.
An attempt was made to investigate the effect of DDAC treatment on wood photodegradation using lignin model compounds. A preliminary study examined the influence of DDAC and ACQ on the photodegradation of vanillin and guaiacol in alcohol-water solutions. No differences were observed for the UV-Vis spectra of vanillin solutions with and without DDAC, before or after UV irradiation. This demonstrated that no interaction took place between DDAC and vanillin in the solution and that the vanillin degradation was independent of DDAC under this experimental condition. However, vanillin could be photostabilized in vanillin-ACQ solution. When ACQ was added to vanillin solution, vanillin displayed a spectrum with the absorption peak at 229 nm shifted to 248 nm while those at 278 and 307 nm were merged to a single peak at 346 nm. DDAC had no influence on the reaction between vanillin and the ammoniacal cupric salt. Similar results were obtained from the photodegradation of guaiacol in solutions. DDAC itself was found to be very stable towards UV irradiation.

Since the major bonding between DDAC and lignin is “ion pairing” and ion exchange (Doyle and Ruddick, 1995), the effect of DDAC on the photodegradation of six lignin model compounds containing different functional groups, was investigated. The degradation of vanillin, 3,4-dimethoxybenzaldehyde, and guaiacol was slowed slightly by increasing the DDAC concentration, but DDAC had no apparent effect on the photodegradation of isoeugenol, 1,2-dimethoxy-4-propenylbenzene, and dehydrogenatediisoeugenol. The catalytic effect of DDAC in wood weathering could not be observed in solution studies due possibly to solvent effects, free radical mobility and the lack of physical and chemical interactions between DDAC and the lignin model compounds in solution. Since the results from studies with LMCs were directly contrast to the
observations recorded for wood, it is not helpful to employ experiments involving DDAC-LMC reactions in solution to examine the mechanisms by which DDAC influences the weathering of treated wood.

The ESR spectra for the DDAC-and DMBC-treated and untreated samples were very similar, consisting of a single peak centered at 3414 G having a g value of 2.0046. The spectral parameters are compatible with those of phenoxy radicals for which a value of g = 2.0046 has been reported. The spectra of all of the DDAC-treated samples showed a sharp increase in free radical formation following photo-exposure. The higher the DDAC retention, the earlier this increase appeared and the greater its relative intensity. This indicated that DDAC behaves as a photosensitizer, and this was confirmed by the ESR spectral shape and g value of the FeCl₃-treated wood, which was comparable to that of the DDAC-treated samples. No sensitization was recorded for the DMBC-treated wood. The relative intensity of unstable free radicals in DDAC-treated samples was higher than that of untreated controls, regardless of DDAC concentration. DDAC had affected the formation and decay of all the free radicals.

When the physically adsorbed DDAC was removed by leaching the wood sample with distilled water, the DDAC sensitization occurred after 48 to 56 minutes of irradiation for the leached samples, compared to 24 minutes of irradiation for the unleached samples. This demonstrated that in wood the fixed DDAC in wood played a dominant role in its sensitization, but the physically adsorbed DDAC could also facilitate the sensitization.
Chapter 7
Conclusions

The fixation study using thin wood sections confirmed that DDAC fixed predominately to lignin and had no significant interaction with cellulose. Copper lignin complexes were formed following ACQ treatment.

The natural weathering studies demonstrated that DDAC treatment accelerated wood weathering by enhancing photodegradation mainly via delignification and demethoxylation. ACQ treatment slowed wood photodegradation by retarding the formation of carbonyl groups and reducing delignification. Cellulose was much less affected than lignin during photo-exposure. The extent of delignification of wood decreased in the order of: DDAC-treated wood > control > ACQ-treated wood. The UV irradiation study showed similar results and further confirmed that the reduced weathering resistance of DDAC-treated wood was caused by the enhanced photodegradation. The photochemical reactions in the laboratory accurately mimicked the photochemical aspects of natural weathering.

A second more comprehensive study of the natural weathering of treated wood confirmed that the wood photodegradation, (i.e. delignification and demethoxylation) was accelerated by DDAC treatment, and slowed by ACQ and CCA treatments. The changes were more pronounced at greater preservative retentions. Comparison of ACQ and CCA treatments indicated that ACQ provided better protection against wood photodegradation. The close relationship of the delignification and demethoxylation rates to the copper
content of ACQ-treated wood, suggested that the light resistance was related to the fixation mechanism of the copper(II). Both ACQ and CCA treatments controlled cellulose degradation. The effect of DDAC on the degradation of cellulose became noticeable after the lignin had been degraded.

Pre-treatment methylation while reducing the effects of weathering, failed to improve the photostability of DDAC-treated wood to match that observed for the untreated controls, suggesting that both fixed and adsorbed DDAC were responsible for the accelerated photodegradation of wood.

The photodegradation of lignin model compounds was independent of DDAC due probably to the lack of interaction between DDAC and the compounds in solutions. However, vanillin could be photostabilized by ACQ, presumably by the formation of a vanillin-copper complex.

The ESR studies of DDAC-treated wood suggested that DDAC functioned as a photosensitizer during the photodegradation of wood, as demonstrated by the spectra of FeCl₃-treated wood. The sensitization takes place via the DDAC-lignin complex, which can promote free radical formation by energy transfer. The effect of DDAC leaching and retention on the free radical formation and decay, suggested that both the physically adsorbed DDAC and the fixed DDAC impact on the formation and decay of the phenoxy free radicals.
References


