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INTERACTIONS OF COPPER-AMINE PRESERVATIVES WITH SOUTHERN PINE

By

Jun Zhang

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Forestry

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ABSTRACT

INTERACTIONS OF COPPER-AMINE PRESERVATIVES WITH SOUTHERN PINE

By

Jun Zhang

The study of the interactions between copper amine preservatives (Cu-EA) and wood substrate is extremely important, since it impacts greatly both on the performance and the environmental consideration of treated wood. The objectives of this research are to investigate copper amine-wood interactions, examine the copper bonding sites and elucidate the copper ethanolamine fixation mechanism. To achieve the objectives, the effects of copper source, amine ligand and amine to copper molar ratio on copper retention and leaching were studied. The copper amine treated wood samples were characterized by FTIR, electron paramagnetic resonance (EPR), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

The results of copper-amine treatment reveal that the retention and leachability of copper in copper amine treated southern pine (SP) are influenced by the formulation and the composition of copper amine treating solutions. The sources of copper used, $Cu(OH)_2$, $CuCO_3$, $CuSO_4$ and $Cu(NO_3)_2$, in the copper amine formulations affect the leachability of copper. Copper amine formulations made from $CuSO_4$ and $Cu(NO_3)_2$ show less copper loss during laboratory water leaching than those from $Cu(OH)_2$ and $CuCO_3$. Increasing amine to copper molar ratio increases the copper retention in wood and the leaching of copper. The nature of amine ligands has some effects on copper retention and

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copper leaching. As the molecular weight of amine ligand increases, the copper loss during leaching decreases.

FTIR analyses show that treatment of SP with Cu-EA causes a significant reduction in the band at 1739 cm^{-1} attributed to carbonyl vibration from carboxylic acid groups and an increase in band at 1596 cm^{-1} from carbonyl in carboxylate. The same result is observed in Cu-EA treated holocellulose. Cu-EA treatment of lignin results in a reduction in the aromatic ester band at 1712 cm^{-1} and an increase in carbonyl from carboxylate at 1595 cm^{-1}. Bands at 1370 cm^{-1} and 1221 cm^{-1}, assigned to phenolic hydroxyl groups, exhibit a decrease in intensity after Cu-EA treatment.

EPR axial spectra are obtained for all Cu-amine treated samples irrespective of the formulations. The values of $A_{||}$ and $g_{||}$ of the axial EPR spectra indicates that the stereo-structure of copper complexes in copper amine treated wood is either tetragonal-based octahedral or square-based pyramidal. Comparison of electronic parameters of $A_{||}$ and $g_{||}$ in Cu-amine treated wood with those of the Cu-amine treating solution and the values reported in the literature suggests that the copper complexes in both treating solution and treated wood are in the form of CuN2O2, where copper is ligated with 2 nitrogen and 2 oxygen in the equatorial plane. XRD does not find any crystalline copper compound in Cu-EA treated wood, and XPS indicates that the valency state of copper in treated wood was cupric.

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ACKNOWLEDGMENTS

This work was made possible only through the help and support of many people. I would like to express my sincere appreciation to Dr. D. Pascal Kamdem, my major professor, for his guidance, patience and friendship. I have learned a great deal from him. His unselfish support and encouragement through my lengthy research program has been greatly appreciated. I would also like to thank the members of my guidance committee Dr. Craig R. McIntyre, Dr. Douglas A. Gage and Dr. Raymond C. Francis for their invaluable suggestions, advice, guidance and constructive critiques of my work. Additionally, I want to thank Dr. Rui H. Huang for helping me with the X-ray diffractometer and Dr. John McCracken for his valuable suggestions in EPR spectrum interpretation.

Successful completion of my research is owed in large part to the other members of the wood science lab: Justin Zyskowski, Maldas Debesh, Weining Cui, Ismail Jusoh, and Wanli Ma. They provided not only moral support, but also a sounding board for ideas and insights for data interpretation.

Funding for this research was provided by the USDA-CSREES Eastern Hardwood Utilization Program in the Department of Forestry at Michigan State University. The continued financial support throughout my research program was gratefully acknowledged.

Finally, but not the least important, my deepest gratitude goes to my wife Hua for her love, encouragement, patience and support during this journey.

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Chapter 1

Introduction

1.1 Overview

Wood, a remarkable material of great importance in the world economy, is widely used as a structural material, fuel, and industrial raw material. However, it is subject to biodegradation through fungal and/or insect attack under a warm and highly humid environment. So, as a renewable natural resource, wood is also biodegradable. The longer it lasts, the less we harvest the forest. Preservative chemicals are commonly used to enhance wood durability. It is estimated that the US industry treated about 727.8 million cubic feet of wood products with chemicals in 1997 (Micklewright, 1998). The preservative treatment increases the service life of wood products by a factor of 10 to 20 times. According to an estimate by the Southern Forest Products Association, pressure treatment of wood material with preservative chemicals saves 226,000,000 trees each year in the US alone. Without the use of preservative-treated wood, the wood fiber demands might have exhausted our forest resources years ago.

Preservative treatment of wood will not only extend its service life under severe outdoor conditions, such as high moisture, oxygen, UV irradiation and insect and fungus attacks, but also improve its market potential in the areas where wood products are facing competition from other polymeric materials. However, some concerns about the use of preservative treated wood are the bioefficacy against fungus and insect attack, and the

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environmental acceptability. As a result, more and more research in the area of wood preservation has been directed to develop new preservatives with acceptable efficacy and low toxicity to humans and environment.

Copper amine is one of the copper-based wood preservative systems. It is used as a source of copper for several new preservative systems including ammoniacal copper quat-type D (ACQ-D), copper dimethyldithiocarbamate (CDDC), and copper azole (AWPA, 1998). Copper amine has gained more and more attention in wood preservation due to its low mammalian toxicity, its fixation ability and the absence of odor. However, relatively little research has been done on the fixation, retention and leaching of copper in copper amine treated wood. The retention and the bonding of copper are considered extremely important because they may influence the performance and the environmental impact of the treated wood products.

Chemically speaking, the copper amine (Cu-EA) system can be water-borne copper complexes in which different amines are used as ligands or chelating agents. Cu-EA is formulated by mixing copper source from copper hydroxide, copper carbonate, copper sulfate or copper nitrate, with aqueous amine ligands. The ligands include mono-ethanolamine (primary amine), 2-methyl-amino-ethanol (secondary amine) and N, N-dimethyl-ethanolamine (tertiary amine). The copper source, amine ligand and ligand to metal ratio may influence the copper retention and leachability of copper in Cu-EA treated wood. In this study, the effects of copper source, amine ligand, and molar ratio of amine to copper on the retention and leaching of copper have been investigated. The fixation mechanism, the bonding sites for copper and the interactions of wood with copper have also been examined.

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1.2 Wood Anatomy and Its Chemistry

Wood is one of the most easily used products. It can be cut and shaped with ease and fastened readily. At the same time, wood is one of the most complex materials. It is made up of specialized tiny cells with defined structure. The anatomical structure and the chemical composition of wood probably influence the interactions between wood and copper-based preservatives.

1.2.1 Anatomical Aspects

Wood is the secondary xylem formed by cell division in the vascular cambium of both softwood and hardwood. Softwood species are known as coniferous trees and hardwood as deciduous trees. Softwood contains relatively simple structure with 90-95% tracheids that are long and slender cells with flattened or tapered closed edges. The tracheids are arranged in radial files, and their longitudinal extension is oriented in the direction of the stem axes. Hardwood has a basic tissue for strength containing fiber, fiber tracheids, vessel and parenchyma. Within the strengthening tissue are distributed conducting vessels, often with large lumina (Fengel and Wegener, 1984). These vessels are long pipes ranging from a few centimeters up to some meters in length and consisting of single element with open or perforated ends.

In all species of wood, the cells composing the axial system and the cells of the ray system are tightly integrated to produce a rigid material. The strength properties of wood are determined by the thickness of the cell walls and the microfibrillar angle of the cellulose component. Additionally, the elongated nature of the axial cells that make up the greatest proportion of the cell types present makes a significant contribution to

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strength. In contrast, the ray cells have little strengthening function either in living trees or in commercial timber because of their radial elongate nature.

Wood cell walls are complex in structure. Most are composed of primary (P) and secondary (S) wall layers. A detailed structure of the cell wall shows that the secondary cell wall is composed of several layers, S1, S2 and S3 with different microfibril orientation. The primary wall, developing first as cells, undergoes differentiation, while the thicker secondary wall is laid down inside the primary wall. Between cells there is a thin layer, the middle lamella (M) which glues the cells together to form tissues. The transition from the middle lamella to the adjacent cell wall layers is not very clear, so a term, compound middle lamella, is used to describe parts encompassing the middle lamella and the two neighbor cell walls (Eaton and Hale, 1993).

1.2.2 Chemical Composition

Major wood components include cellulose, hemicellulose and lignin. Cellulose is the most abundant component of wood and constitutes slightly less than one-half of the wood in both hardwood and softwood. The proportion of lignin and hemicellulose varies widely among species and between hardwood and softwood. Table 1.1 shows the approximate percentage of dry weight of each in hardwood and softwood. In addition, wood also contains small amount of extractives that may vary from 0 to 10%.

1.2.2.1 Cellulose

The structure of cellulose was thoroughly surveyed by Purves (1954), and Marchessault and Sundararajan (1983). Cellulose is present as the main structural component in wood cell walls in the form of microfibrils. The cellulose microfibrils

Table 1.1 Percentage of wood components in cell wall (Haygreen and Bowyer, 1996)

Type	Cellulose	Hemicellulose	Lignin
Hardwood	40-44	15-35	18-25
Softwood	40-44	20-32	25-35

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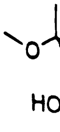
Cellulose is a polydisperse linear natural polymer. The basic monomeric unit of cellulose is D-glucose, which is linked through glycosidic bonds in the beta configuration between carbon 1 and carbon 4 of adjacent units to form a long chain of 1, 4-β-linkages (Figure1.1). Each β-D-glucopyranose unit within a cellulose chain has three types of hydroxyl groups, one primary (C_6-OH) and two secondary (C_2-OH and C_3-OH). The hydroxyl groups frequently form intra- and inter-molecular hydrogen bonds within and among molecules. These bonds, together with other secondary force, such as Van der Waals force, aggregate portions of the molecular chains into various degrees of lateral order ranging from perfect geometrical packing of the crystal lattice (the so-called crystalline region) to the random fraction (amorphous region).

Although there are OH-groups at both ends of the cellulose chains, these OH-groups show different behaviors. The C1-OH is an aldehyde hydrate group deriving from the ring formation by an intra-molecular hemiacetal linkage. This is why the OH-groups at the C1-end have a reducing property, while the OH-groups at the C4-end of the cellulose chains are alcoholic hydroxyl and therefore non-reducing. The topochemistry of cellulose actually controls the chemical reactivity of cellulose. Essentially, the hydroxyl groups located in the amorphous regions react readily in many chemical reactions. In the crystalline regions, where there are close packing and strong inter-chain bonding, the hydroxyl groups are not readily accessible to reactant.

1.2.2.2 Lignin

Next to cellulose, lignin is the most abundant and important polymeric organic substance in wood. It exists as one of the essential wood components ranging in amount



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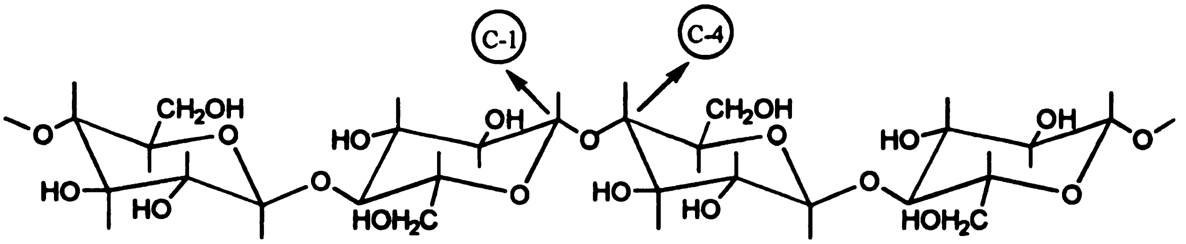

Figure 1.1 Stereo-chemical structure of cellulose (Fengel and Wegener, 1984)

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from 20 to 30% (Fengel and Wegener, 1984). The distribution of lignin within the cell wall and the lignin content in different parts of a tree are not uniform. It is thought that lignin is a polymer formed by the enzymatic dehydrogenation of phenylpropanes followed by radical coupling (Eaton and Hale, 1993). Softwood lignin is mainly composed of guaiacyl units originating from the predominant precursor, trans-coniferyl alcohol (Figure 1.2b), while hardwood lignin is composed of both guaiacyl and syringyl units derived from trans-coniferyl and trans-sinapyl alcohol (Figure 1.2c). Analysis of structural elements of lignin demonstrates that carbonyl groups in lignin exists in different types including aldehydes, unconjugated ketones, conjugated ketones and carboxyl groups. The phenolic groups and aliphatic hydroxyl groups of lignin have been quantitatively determined by various methods (Sarkanen and Schuerch, 1955; Adler and Hernestam, 1955; Robert and Brunow, 1984).

Ultraviolet (UV) spectroscopy, particularly when used along with chemical modification, has contributed to estimating the frequencies of functional groups and linkage types. Lignin shows a strong absorption spectrum in the UV region because of its aromatic nature. In general, softwood lignin shows a maximum absorption at 280-285nm, and hardwood lignin at 274-276nm (Terashima, 1978). Aulin-Erdtman (1963) and Aulin-Erdtman and Sanden (1968) applied UV spectroscopy to estimate effectively the amounts of the phenolic hydroxyls of lignin.

Infrared spectroscopy has also been used for the characterization of lignin, and the major absorption band frequencies and the most probable assignment of each band in guaiacyl and guaiacyl-syringyl lignins have been summarized by Hergert (1971). The absorption bands at 1605-1595 cm^{-1}, 1515-1505 cm^{-1}, and 1450-1420 cm^{-1} are assigned to

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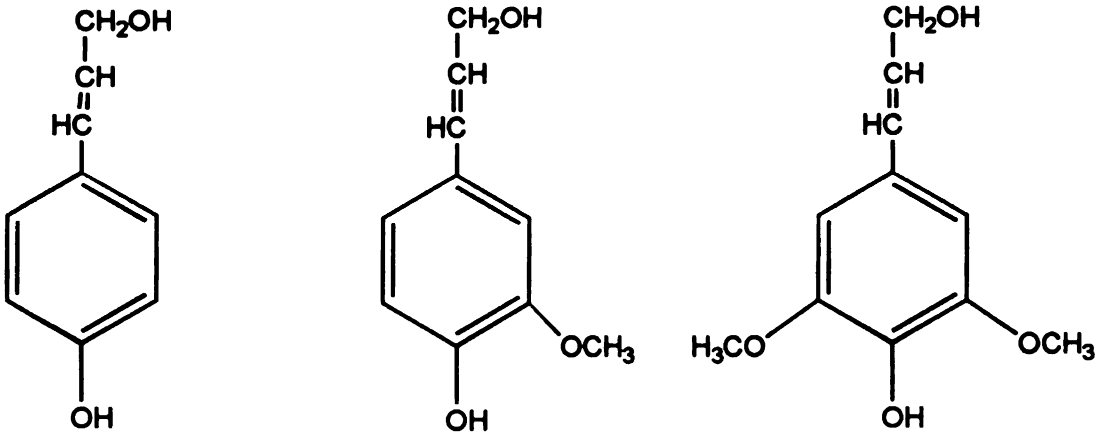

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Figure 1.2 The building units of lignin: (a). p-coumaryl alcohol, (b). coniferyl alcohol and (c). sinapyl alcohol (Fengel and Wegener, 1984)

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aromatic skeletal vibration. IR spectroscopy has also been used to estimate the content of lignin (Kolboe and Ellefsen, 1962) and the ratio of syringylpropane to guaiacylpropane units in hardwood lignin (Sarkanen *et al.*, 1967a and b). The lignin content was estimated by the difference of spectra between the original wood and holocellulose at 1515 cm^{-1}, and gave 28% to 29% that is in agreement with other estimations (Fengel and Wegener, 1984). Sarkanen *et al.* (1967a and b) compared the spectra of specifically deuterated guaiacyl and syringyl model compounds with those of undeuterated lignin models, and gave several new band assignments. The 1340-1380 cm^{-1} and 1250-1150 cm^{-1} absorption bands were assigned to phenolic hydroxyl groups.

The magnetic resonance spectroscopic tool is very useful in lignin chemistry research. The first ^{1}HNMR spectra of lignin and its model compounds were obtained by Ludwig *et al.* (1964a and b). The chemical shifts of the NMR signals from protons in various model compounds have been determined (Ludwig *et al.*, 1964 b). The NMR of dehydrodiconifyl alcohol indicates a cis-configuration in its furan ring and the diequatorial configuration of pinoresinol (Ludwig *et al.*, 1964a and b). Lüdemann and Nimz (1974) studied the ^{13}CNMR spectra of lignins. The chemical shifts of various carbons in lignin model compounds, and the effect on the chemical shifts of the aromatic carbon atoms from methoxyl ortho to the 4-phenolic hydroxyl group were examined.

1.2.2.3 Hemicellulose

The chemistry of hemicelluloses (polyoses) has been reviewed extensively by Aspinall (1959) and Timell (1964 and 1965). Hemicelluloses differ from cellulose in the composition of various sugar units, molecular chains and branching of the chain molecules. The basic sugar units making up the hemicelluloses are grouped into categ

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categories such as pentoses, hexoses, hexuronic acids and deoxy-hexoses (Fengel and Wegener, 1984). The sugar units contain glucose, mannose, galactose, xylose, and arabinose. Softwood and hardwood differ in the different percentages of total hemicelluloses but also in the percentage of individual polyoses and composition of these polyoses. Softwood tends to have a higher proportion of mannose and galactose units than hardwood, while hardwood has a higher proportion of xylose units and more acetyl groups than softwood.

1.3 Wood Deterioration

Wood products, when used out of doors, are subjected to decay, fungal stains, and insect infestation, all of which cause the deterioration of wood. Biological agents are the major causes of wood deterioration. The greatest financial losses from biodeterioration result from wood decay fungi. These fungi feed on the compounds of the cell wall and consequently weaken the structure of the wood to such an extent that wood breaks. Wood destroying fungi can be classified into three categories, namely brown rots, white rots and soft rots.

The brown rots selectively attack the cellulose and hemicellulose of the cell and leave the darker lignin more or less intact. Wood, after attack, seriously degraded and remained an abnormally brownish color. The surface can become badly broken by deep transverse and longitudinal cracks. The most common brown rots are often found attacking softwood timbers and the lighter hardwoods.

In the white rot type of fungi, the fungi have the ability to degrade both the lignin and cellulosic components of the cell although the lignin is usually decayed at a faster

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rate. The affected wood eventually becomes much lighter in color and weight, and loses its strength properties. White rotted wood usually retains its shape but may eventually become a fibrous spongy mass.

Soft rot fungi most often attack wood that is wet or contact with ground. The physical and chemical character of the form of wood cell attack caused by this type of fungi differs markedly from that of the above two types of fungi. Decomposition commonly results from the organism making longitudinal cavities in and parallel to the axis of the cell wall. In wet wood, the presence of soft rot is evident if surface layers are soft and may be readily scraped away. Hardwoods are thought to be naturally more susceptible to soft rots than softwoods though no wood is completely resistant.

In addition to wood destroying fungi, some other agents that affect wood properties are staining fungi, moulds, wood borers, termites and so forth. The existence of all these factors could dramatically reduce the service life of wood products. Essentially, Fungicide is widely used to protect wood products from deterioration.

1.4 Role of Copper as a Fungicide

Many fungicidal chemicals used as wood preservatives interfere with respiration either by inhibiting the formation of acetyl coenzyme A (CoA) or by interrupting respiratory chain phosphorylation (Eaton and Hale, 1993). The mode of fungicidal activity of copper-based wood preservatives is assumed to involve metal-enzyme interactions, generation of highly reactive free radical by copper ions, and the modification of DNA (Hertzberg and Dervan, 1984).

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Divalent cations of the first transition series, such as Cu^{2+}, can inhibit the oxidative activity of alcohol dehyogenase 1 (ADH1) from *Saccharomyces cerevisiae* (Gastaldi *et al.*, 1993). Copper ions interact with both enzyme-cofactor (ECI) and enzyme-cofactor-substrate (ECIS), which produce the enzyme-inhibitor complex and the enzyme-substrate-inhibitor complex (Gastaldi *et al.*, 1993).

Superoxide radicals ($O_2^{\cdot -}$) and H_2O_2 are produced in many biological systems. These are relatively harmless as they react with biomolecules at low rates, and specific enzymes exist to remove them (Simpson *et al.*, 1988). Free Cu^{2+} ions are expected to catalyze the conversion of $O_2^{\cdot -}$ and H_2O_2 to the hydroxyl radical ($OH^{\cdot}$) which is known to be highly reactive (373 kJ mol^{-1}). The formation of hydroxyl radical leads to uncontrolled oxidation processes (Hartmann and Weser, 1977; Peisach and Blumberg, 1969; Simpson *et al.*, 1988). For this reason, biological cells usually keep metal ions very firmly bound in less reactive forms (Halliwell and Gutteridge, 1986). The reactions of cupric salts with H_2O_2 and $O_2^{\cdot -}$ are as follows:

$$Cu^{2+} + H_2O_2 \longrightarrow Cu^{+} + HO_2^{\cdot} + H^{+}$$

$$Cu^{+} + H_2O_2 \longrightarrow OH^{\cdot} + OH^{-} + Cu^{2+}$$

$$Cu^{2+} + O_2^{\cdot -} \longrightarrow Cu^{+} + O_2$$

$$Cu^{+} + O_2^{\cdot -} \longrightarrow Cu^{2+} + H_2O_2$$

The presence of free cupric ions induce the generation of highly reactive hydroxyl radical ($OH^{\cdot}$). The hydroxyl radical can damage the protein molecules (Hunt *et al.*, 1988; Kobayashi *et al.*, 1990). Hydroxyl radical attacks both the deoxyribose sugars arrayed

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along the surface of DNA (Hertzberg and Dervan, 1984) and the bases of which are constructed the DNA molecules (Inoue and Kawanishi, 1987). As a fungicide, cupric copper ion (valence state is 2+) is effective, because it can induce the generation of highly reactive free radical which damages the DNA and enzyme (Hunt *et al.*, 1988; Hertzberg and Dervan, 1984).

1.5 Interactions of Wood with Copper-Based Wood Preservatives

The interactions of wood and copper-based preservatives impact both the performance and the environment aspects of treated wood. In the last few decades, the chemical and/or the physical interactions between copper-based wood preservatives and wood components have been extensively studied (Dahlgren, 1972; Dahlgren and Hartford, 1972; Pizzi, 1981 and 1982; Cooper, 1991 and 1998; Ostmeyer *et al.*, 1988 and 1989). Many researchers in wood preservation area have attempted to determine the fixation mechanisms of copper and predict its retention and migration in wood (Cooper, 1991 and 1998; Kamdem and McIntyre, 1998; Craciun and Kamdem, 1997; Pizzi, 1981 and 1982).

1.5.1 Ion-Exchange Theory

Wood contains various ionizable functional groups. Hemicelluloses carry carboxylic acid groups, which can be ionized in neutral or weakly acidic conditions. Lignin contains phenolic groups, which can be ionized at pH above 10. Cellulose contains alcoholic hydroxyl groups, which are ionized only in very strong base (pH above 15) (Sjöström, 1989). All these functional groups are potential ion exchange sites when wood is treated with preservatives containing metal ions.

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Ion exchange is usually defined as a fast reaction. Dahlgren (1972) and Dahlgren and Hartford (1972) performed extensive studies on CCA fixation in sapwood from pine and spruce. They found that the H^+ activity of the CCA was lowered to less than 20% of that in the original solution within the first 3 minutes, and they attributed this phenomenon to ion exchange occurring between wood components and copper/ chromium cations. Other studies also suggested that the copper absorption by wood through cation exchange appeared to be instantaneous after treatment (Eadie and Wallace 1962; Gray and Dickinson, 1988; Wilson, 1971).

The pH value of the treating solution plays a critical part in ion exchange. The ion exchange capacity of wood depends on the pH of the treating solution. The pH controls the dissociation of weak acid groups in wood. The acid groups in wood have different pKa values. The carboxylic groups have a pKa of around 4, the phenolic groups 10-12, and the alcoholic groups 13-15 (Sjöström, 1989). The amount of adsorbed copper during CCA treatment increases as the pH increases (Gray and Dickinson, 1988; Pizzi, 1983). At lower pH or neutral conditions, carboxylic acid groups in wood are dissociated. The carboxylic acid groups in hemicelluloses of the wood cell wall (uronic acids) are mainly responsible for cation exchange (Rennie *et al.*, 1987; Cooper, 1991; Knight *et al.*, 1961; Mitchie, 1961). As the pH increases to above 10, the phenolic groups in lignin may become dominant sites responsible for ion exchange (Rennie *et al.*, 1987; Pizzi, 1982). Lebow and Morrell (1993) reported that phenolic groups from wood extractives also provided ion exchange sites for copper, which caused high copper adsorption in the heartwood of Douglas fir. At high pH above 15, even alcoholic groups can provide additional ion exchange sites (Rennie *et al.*, 1987).

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Chen *et al.* (1996) suggested that ion exchange adsorption of metal ions can be characterized using Langmuir's adsorption equation (Adamson, 1990) or Freundlich adsorption isotherm (Freundlich, 1926). Mitchie (1961) and Pizzi (1981) used Langmuir's monolayer adsorption isotherm to describe the adsorption of copper and chromium on wood. Cooper (1991 and 1998) conducted extensive research on ion exchange adsorption of various copper-based preservatives on wood and concluded that Langmuir's monolayer adsorption isotherm equation correlates well the experimental data of copper adsorption.

1.5.2 Copper Forms in Treated Wood

Several commercial inorganic wood preservatives contain copper because of its excellent fungicidal characteristics. Although tremendous efforts have been directed to investigate the chemical interactions and the performance of copper based preservatives with wood, the forms of copper and the structure of copper complexes or precipitates in wood are not well documented. Copper might be present in treated wood as copper-cellulose complex, copper-lignin complex, and crystalline or amorphous inorganic/ organic copper compounds. Knowledge of these forms of copper is of great importance because it may lead to improve the fixation process, the leaching resistance and the biological efficacy.

Belford *et al.* (1957, 1958) reported that metallic salts reacted with cellulose to form metallo-cellulose complexes when wood was impregnated with aqueous solutions of copper sulfate and copper sulfate-potassium dichromate mixtures. Hulme (1979) proposed the formation of copper-cellulose complex as a result of hydrogen bonding. Kubel and Pizzi (1982) studied the reactions of CCA with cellulose and its model

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compounds. They observed an initial absorption of copper on cellulose and postulated that the absorption was physical in nature.

Bland (1963) reported that copper was concentrated in the region of the compound middle lamella and suggested that lignin was a significant bonding site for copper. Studies by other researchers also provided evidence that lignin plays a significant role in absorbing copper (Gray and Dickinson, 1988; Rennie *et al.*, 1987). Pizzi (1982) reported that copper might complex with ortho-dihydroxy phenols and ortho-hydroxy-methyl phenols in wood after CCA treatment. Using lignin model compounds and ammoniacal copper preservatives, Xie *et al.* (1995) proposed that the formation of copper lignin complex was a key reaction during fixation. Lebow and Morrell (1995) investigated the interactions of ACZA with Douglas fir and suggested that phenolic hydroxyl groups provided primary reaction bonding sites for copper. Daniel and Nilsson (1987) observed that syringyl lignin had low copper retention and suggested that CCA reacted preferentially with guaiacyl lignin.

The reaction between copper ion and carboxylic acid has also been studied. Bayley (1960) suggested the formation of metal organic complexes that resulted from the reaction of metal ions with the acid groups of non-cellulosic constituents of wood. Craciun *et al.* (1997) proposed that copper ion reacted with carboxylic acid groups to form copper carboxylate when wood was treated with copper preservatives. Thomason and Pasek (1997) reported that the adsorbed copper decreased when the acid groups in wood were reduced by heating, and concluded that adsorbed copper was bound to the carboxylic acid groups within hemicellulose. Other studies (Pizzi, 1993a and 1993b) on the inte

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the interaction mechanism showed the same findings when copper based preservatives were used for wood impregnation.

The formation of inorganic copper precipitates also plays an important role in copper fixation. In CCA fixation, precipitation reactions occur after the initial ion exchange and adsorption (Pizzi, 1981 and 1982). Pizzi (1981 and 1982) postulated that most of CCA becomes copper chromates or chromium arsenate that either complexed with lignin or physically precipitated into the cellulose as inorganic salts. In addition, Dahlgren and Hartford (1972) reported the precipitation of copper arsenates. In ACZA fixation, copper forms inorganic compounds through precipitation as the ammonia evaporates from the wood (Hulme, 1979; Jin and Archer, 1991). Lebow and Morrell (1995) reported that the majority of copper precipitated in the wood was in the forms of copper carbonates, copper oxides, or copper arsenate compounds. The fixation of copper in the copper dimethyldithiocarbamate (CDDC) system is mainly ascribed to the formation of CDDC crystals. Reaction of copper ethanolamine and sodium dimethyldithiocarbamate (SDDC) leads to an insoluble copper dimethyldithiocarbamate chelate with a 1:2 molar ratio of copper to dithiocarbamate (Cooper and Stokes, 1993; Kamdem and McIntyre, 1998).

1.5.3 Physiochemical Analysis of Copper-Based Preservative Treated Wood

Many researchers have employed physiochemical analysis to study the fixation chemistry of copper on wood (Ostmeyer *et al.*, 1988 and 1989; Hughes *et al.*, 1992 and1994; Craciun and Kamdem, 1997; Kamdem *et al.*, 1991; Kamdem and McIntyre, 1998; Ruddick *et al.*, 1992). In a study of fixation of copper ammoniacal system, Xie *et al.*(1995) used Electron paramagnetic resonance (EPR), X-ray diffraction (XRD), and

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Fourier transform infrared spectroscopy (FTIR) to examine the structure of the complex formed by reaction of copper solution with a lignin model compound, vanillin. Ostmeyer *et al.* (1988 and1989) used X-ray photoelectron spectroscopy (XPS) and diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) to evaluate CCA treated Southern pine. They concluded that the carbon-hydrogen bonds of the aromatic rings were oxidized with possible formation of hexavalent chromate esters. Other studies by Yamamoto and Ruddick (1990) did not provide evidence of the oxidation of hydroxyl groups to carbonyl groups.

The reaction of preservative with wood components should result in the formation of new chemical bonds. FTIR can be used to determine the formation of new bonds by comparing sample spectra before and after treatment. Michell (1993) used FTIR to study the reaction of wood and of lignin model compounds with inorganic chromium trioxide and concluded that inorganic preservatives reacted with wood via the aromatic ring of lignin. In an FTIR study of CDDC treated wood, Craciun *et al.* (1997) postulated that the wood/Cu-complex interaction occurred partially through a ligand exchange reaction between wood carboxylate groups and 2-ethanolamine of the copper complex.

Since Cu^{2+} is paramagnetic, electron paramagnetic resonance spectroscopy (EPR) can be used to investigate the bonding environment or the modification of copper complexes in treated wood samples. Placket *et al.* (1987) used EPR to study Radiata pine treated with CCA and copper sulfate. They observed no evidence of a copper-lignin complex, but rather that copper ions appeared to be hydrated and stored within fixed sites of the wood. The forms of copper present in *Pinus sylvestris* treated with copper based preservatives were analyzed using EPR by Hughes *et al.* (1994). The authors found that

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immobile Cu^{2+} with anisotropic configuration existed in all treated wood samples irrespective of formulation. They further suggested that copper was complexed with 3 or 4 nitrogens in copper amine treated wood and copper was complexed with four oxygen in a distorted octahedral configuration in nitrogen free systems.

Like EPR, XPS is another useful tool, which can be performed directly on the treated sample. Craciun and Kamdem (1997) applied XPS, along with FTIR, to study the waterborne copper naphthenate wood preservatives. They found that a copper complex was formed through the interaction of copper ion from the treating solution and carboxylic and/or carbonyl groups of wood. The oxidation state of copper present in treated wood was as Cu^{2+} ion.

XRD is a non-destructive technique and can be used to examine treated wood. It can be used to identify and quantify crystalline compounds present in a matrix. Creely *et al.* (1978) used XRD to study the complexes of cellulose with secondary diamines. The interaction of wood with inorganic solvents was studied with XRD by Shiraishi *et al.* (1975). Craciun *et al.* (1997) used XRD to identify CDDC crystal formation in CDDC treated wood. Sutter *et al.* (1983) confirmed the formation of copper oxalate in wood treated with a copper-based preservative by using XRD. Kamdem *et al.* (1997) observed the formation of a crystal and identified it as cuprous oxide using XRD.

1.6 Chemistry of Copper-Amine Wood Preservative System

Although the copper amine system as a wood preservative is fairly new in the wood preservation area, researchers in the area of inorganic chemistry have studied copper amine chemistry for a long time. The copper amine system is copper complexes

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with different types of amines as ligands or chelating agents. So far, most research has been centered on copper ethanolamine complexes in which ethanolamines act as bidentate ligands through amino and hydroxyl groups (Davis and Patel, 1963; Hancock, 1981; Djurdjevic and Bjerrum, 1983). Copper monoethanolamine was first studied by Davis and Patel (1963). They performed conductimetric and potentiometric titration to investigate the structure of the resulting chelating complex. They observed that cupric salts reacted with monoethanolamine to form a non-conducting complex under high pH, and diethanolamine and triethanolamine behaved similarly. The formation constants of copper ethanolamine complexes in water were determined (Davis and Patel, 1968; Djurdjevic and Bjerrum, 1983). The formation constants of copper ethanolamine complexes vary with the pH of the solution. Hancock (1981) pointed out that deprotonation of alcoholic group occurred with high pH by conducting a glass electrode study of the complexes of ethanolamine with Cu(II). His findings were later confirmed by Tauler and Casassas (1986). Electronic spectra of cupric ethanolamine solution show that a higher number of ligands leads to the formation of more stable complexes (Hancock, 1981). Using ESR, Tauler and Casassas (1986) observed four species of copper monoethanolamine with the stoichiometries1-1-0, 1-2-0, 1-2-1, 1-2-2, where the first two digits represent the numbers of metal and ligand, respectively, and the last digit the numbers of proton released. Jensen (1971) used UV spectroscopy to identify the coordinated alcoholate in copper monoethanolamine complexes dissolved in organic solvents, and estimated the acidic constant of the alcohol group of the ligand. Research by Casassas *et al.* (1989) demonstrated that at pH below 12 mono- and di-ethanolamine can forr

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can form four species by stepwise addition of two molecules of the ligand to the metal followed by deprotonation of two hydroxyl groups.

In the visible spectra of the aqueous copper-ethanolamine system, Ojima and Sone (1961) observed a band at 520 nm. This band increases in intensity as a function of the molar ratio of the aminoalcohol to copper, or when strong base (pH above 12) was added to the system. This band was assigned to the formation of the deprotonated copper amine species. The molecular and electronic structure of the $CuCl_2$-complexes with monoethanolamine and triethanolamine in solid and in DMF solutions was examined with EPR (Hedewy, 1986). The results indicated that a dimeric structure of $CuCl_2$-aminoethanolate complexes with very weak Cu-Cu coupling, and the $CuCl_2$-aminoethanolate complexes were influenced by the molecules of solvent. Kadoshnikova (1991) conducted research on precipitating residual cupric ion from aqueous solutions of copper nitrate by adding ethanolamine into the solution. The amount of copper in solid precipitate varies with the molar ratio of amine to copper. Copper precipitate increases as the initial molar ratio increases. Further increase in the molar ratio of amine to copper (above 1.6) leads to the dissolution of the solid phase as a result of complex formation. Hancock (1981) and Handcock and Nakani (1984) reported that an unsubstituted alkylamine, such as ethylamine, precipitated the hydroxide when added to cupric solutions because of the steric hindrance to coordination caused by the alkyl group.

The stability and structure of complexes vary with the pH values, copper to amine molar ratio and solvent molecules. The formulation of copper-amine complexes should consider all these parameters for the stability and the efficacy.

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1.7 Objectives

The objectives of this study are to examine the physical and chemical interactions between copper-amine wood preservatives and Southern pine, and provide a feasible mechanism for copper fixation in copper-amine treated wood. To achieve the objectives, solid techniques, such as FTIR, EPR, XRD and XPS, will be applied to study the copper amine treated wood samples.

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Chapter 2

Effect of Copper-Amine Composition on Copper Absorption and Leaching

2.1 Abstract

The absorption and leachability of copper in copper amine (Cu-EA) treated wood were influenced by the formulation of the copper amine treating solutions. The sources of copper used, $Cu(OH)_2$, $CuCO_3$, $CuSO_4$ and $Cu(NO_3)_2$, in the copper amine complex formulation affected the leachability of copper. Data showed that copper amine from $CuSO_4$ and $Cu(NO_3)_2$ treated wood had less copper loss during laboratory water leaching than from $Cu(OH)_2$ and $CuCO_3$ treated wood. Increasing the amine to copper molar ratio increased the copper retention by wood, but reduced the leaching resistance of copper. The types of amine ligand, such as monoethanolamine (primary amine), 2-methylamino-ethanol (secondary amine) and N, N-dimethyl-ethanolamine (tertiary amine), had some effect on copper retention and copper leaching. As the molecular weight of amine ligands increased, copper loss during leaching decreased.

2.2 Introduction

More and more research in the area of wood preservation has been directed in the development of environmentally benign preservative systems with low mammalian toxicity and acceptable efficacy. The copper amine system is one of the new emerging copper-based preservatives that are receiving a lot of attention. It is one of the main

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ingredients of ammoniacal copper quat-type D (ACQ-D), copper dimethyl-dithiocarbamate (CDDC), and copper azole (AWPA, 1998).

The fixation mechanism of copper in chromated copper arsenate (CCA) and ammoniacal system has been extensively studied. The effect of formulation on the efficacy and performance, the fixation chemistry and the reaction kinetics of copper ion in CCA treated wood have been greatly examined (Fahlstrom *et al.*, 1967; Hagar, 1969; Dahlgren and Hartford, 1972; Pizzi, 1982). The general theory of fixation of copper in an ammoniacal system is that the cupriammonium ion is fixed through cation adsorption reactions with the wood substrate and through precipitation of copper inorganic compounds (Hulme, 1979; Jin and Archer, 1991). Hartford (1972) suggested that insoluble copper precipitates were formed after the evaporation of ammonia in solvent. Lebow and Morrell (1993) proposed that the phenolic wood extractives provided reactive sites for copper fixation in ACZA treated wood.

While the fixation mechanisms of other copper-based wood preservatives have been widely studied, relatively little research has been done on the fixation, retention and leaching of copper in copper amine treated wood. It is reasonable to presume that the copper source, the amine ligand and the ligand-metal molar ratio influence the copper fixation in copper amine treated wood. In this study, the effects of copper source, such as copper sulfate, copper nitrate, copper carbonate and copper hydroxide, the amine ligand, such as monoethanolamine (primary amine), 2-methylamino-ethanol (secondary amine) and N, N-dimethyl-ethanolamine, and the amine to copper molar ratio on the retention and the leaching of copper in treated wood were investigated.

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2.3 Materials and Methods

2.3.1 Formulation of Copper Amine (Cu-EA) Treating Solutions

To evaluate the effect of different copper sources on wood-copper interaction, four different copper compounds, namely, copper hydroxide, copper carbonate, copper nitrate and copper sulfate, were used in copper amine formulations. Copper amine treating solutions were made up by mixing these copper compounds with an aqueous solution of monoethanolamine (MEA). The molar ratio of amine to copper was set at 4.

To evaluate the effect of amine ligands on copper fixation, copper amine treating solutions were prepared by mixing copper hydroxide with three different ethanolamines including a primary amine monoethanolamine (MEA), a secondary amine 2-methylamino-amine (MeEA), and a tertiary amine N, N-dimethyl-ethanolamine (DMeEA). The amine to copper molar ratio was set at 4.

To evaluate the effect of amine to copper molar ratio on copper fixation, copper amine treating solutions were formulated by mixing copper hydroxide and MEA, MeEA and DMeEA at a molar ratio of amine to copper varying from 3 to 8.

2.3.2 Treatment

Defect-free 5 by 10 by 180cm (2 by 4 inch by 6 feet) kiln-dried sapwood boards of Southern pine (SP) were used in this study. Cubes measuring 19mm (0.75 inch) were prepared from these boards and stored in a conditioning room maintained at 65% relative humidity (RH) and 20 °C (68 °F) until they reached an equilibrium moisture content (EMC) of 12 ± 3%. The conditioned cubes were then pressure-treated with copper amine solutions. The copper contents in the solutions were 0, 0.25, 0.5, .075 and 1.0% by weight. The treating procedure included an initial vacuum at 84.6 kPa (25 inch Hg) for 5 minute

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minutes, followed by a pressure level of 690kPa (100 psi) for 1hour, and then a final vacuum for 10 minutes. Treated samples were conditioned at room temperature for 2 weeks before further test. The copper contents in treated wood samples were analyzed by using a Perkin-Elmer atomic absorption spectrometer (AAS) model 3110, as described in the AWPA standard (AWPA, 1998).

2.3.3 Leaching

After the conditioning of treated cubes, the leaching test was carried out to determine the amount of copper leached from treated wood. Three treated wood cubes weighing 10 grams were placed in a 200ml flask and immersed in 100ml deionized water. The flasks were positioned on a horizontal-shaking tray with continuous mild shaking, and an equal amount of fresh deionized water was renewed every day for 8 days. The copper content in water leachate and in leached cubes was analyzed by AAS.

2.4 Results and Discussion

2.4.1 Effect of Copper Sources

AAS analyses indicated that the source of copper influenced the level of copper absorbed during the treatment of Southern pine with Cu-EA (Figure 2.1). At lower concentration of copper in solution (about 0.25%), no significant difference was observed for the level of copper absorbed by wood for all copper sources. As the copper concentration increased, more copper was absorbed. Solutions made from copper hydroxide and copper carbonate yielded higher copper retention levels than those made from copper sulfate and copper nitrate. The pH of the treating solutions is tabulated in Table 2.1. It is noticed from Figure 2.1 and Table 2.1 that the retention of copper in wood

Figure 2.1 Effect of copper sources on copper retention. Copper amine solutions were made by mixing monoethanolamine with difference copper sources

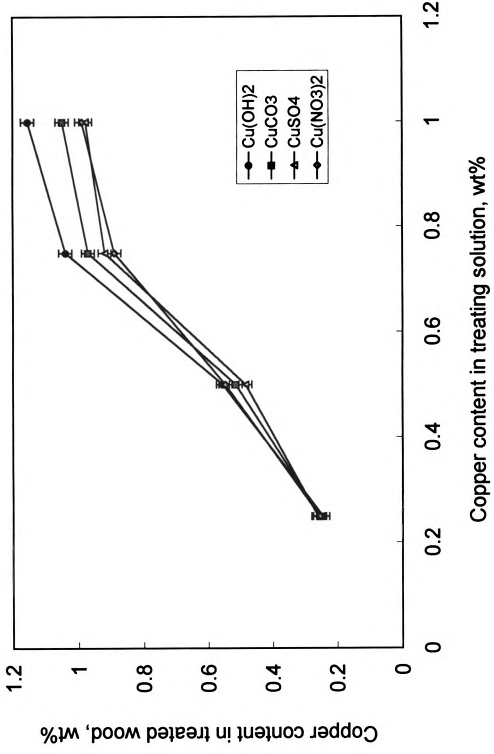
Copper content in treated wood, wt%
1.2
1
0.8
0.6
0.4
0.2
0
Copper content in treating solution, wt%
0
0.2
0.4
0.6
0.8
1
1.2
Cu(OH)2
CuCO3
CuSO4
Cu(NO3)2

Figure 2.1

Table

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Cu
Cu
Cu
Cu

Table 2.1 pH of copper monoethanolamine treating solutions from different copper compounds with amine to copper molar ratio of 4

Copper compounds	Copper concentration in solution (wt %)			
	0.25	0.5	0.75	1.0
Cu(OH)2	10.6	10.8	10.8	10.8
CuCO3	10.0	10.1	10.2	10.3
CuSO4	9.2	9.3	9.3	9.3
Cu(NO3)2	9.1	9.1	9.1	9.1

increases as the pH of treating solutions increases. High pH solution systems resulted in higher copper absorption. These findings generally agree well with the previous study reported by Cooper (1998). A high pH solution might increase the dissociation of carboxylic and phenolic groups, which in turn promote the retaining ability of copper.

Copper source also plays an important role in copper leaching resistance (Figure 2.2). After an 8-day water leaching of wood cubes treated with 0.5% copper solution, about 12% copper from copper hydroxide system was lost, 10% from copper carbonate, 7% from copper sulfate and 6% from copper nitrate (Figure 2.2). The copper leaching resistance shows an opposite trend to copper absorption. Copper from copper sulfate and copper nitrate is more leaching resistant than copper from copper hydroxide and copper carbonate. For copper amine complexes, high pH solution systems lead to higher copper retention, and higher copper loss during leaching (Figure 2.2 and Table 2.1).

2.4.2 Effect of Amine Ligands

The role of amine ligands in copper fixation is important because ligands can affect the stability, polarity, and solubility of copper amine complexes. Figure 2.3 illustrates the influence of ligands on copper absorption. As the molecular weight of the amine ligands increases, less copper is absorbed. Cu-EA made with primary amine (MEA) solution system resulted in higher level of copper absorption than those made from secondary amine (MeEA) and tertiary amine (DMeEA). As the copper concentration of treating solution increases, this tendency becomes more noticeable.

Figure 2.4 shows the result of laboratory water leaching test on different copper amine treated wood samples. It is noted that amine ligands influence copper leachability significantly. As the molecular weight of amine increases, the leaching resistance of

Figure 2.2 Effect of copper sources on copper leaching from copper amine treated samples. (——) 1.0% copper treated; (┈┈) 0.5% copper treated

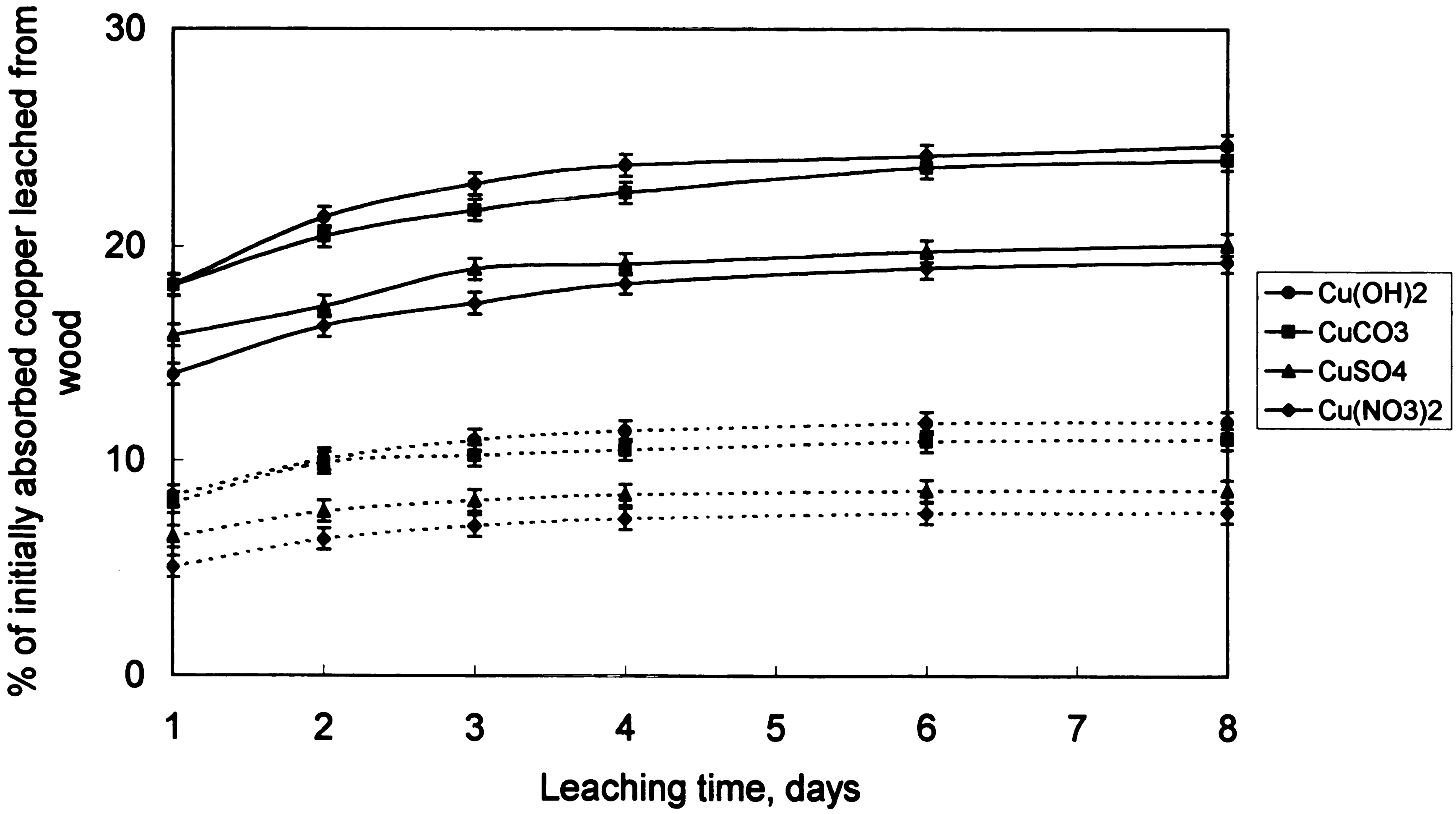

% of initially absorbed copper leached from wood
30
20
10
0
1
2
3
4
5
6
7
8
Leaching time, days
Cu(OH)2
CuCO3
CuSO4
Cu(NO3)2

Figure 2.2

Figure 2.3 Effect of amine ligands on copper retention. Copper amine solutions were made by mixing copper hydroxide with different amines

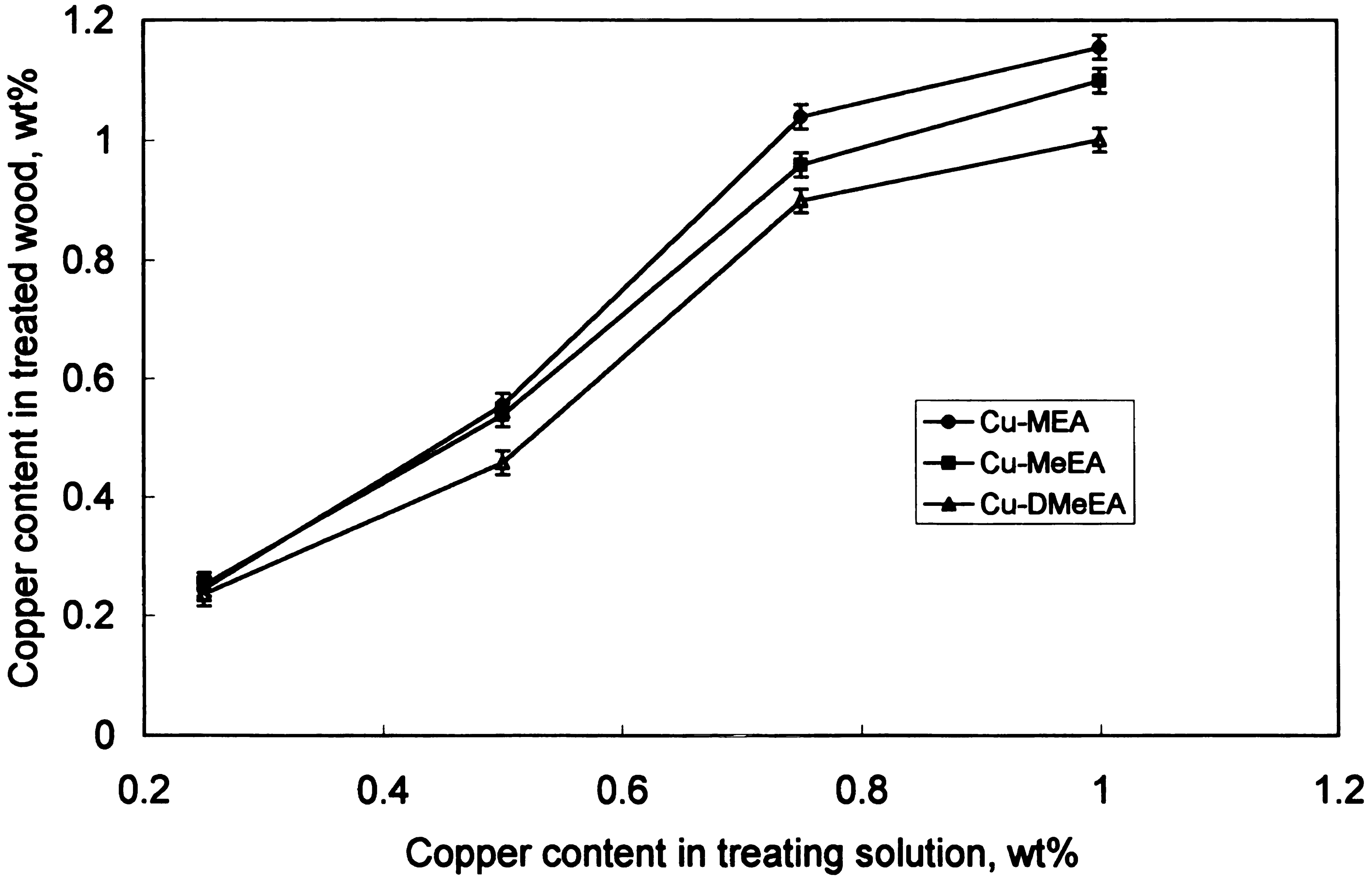

Copper content in treated wood, wt%
1.2
1
0.8
0.6
0.4
0.2
0
0.2
0.4
0.6
0.8
1
1.2
Copper content in treating solution, wt%
Cu-MEA
Cu-MeEA
Cu-DMeEA

Figure 2.3

Figure 2.4 Effect of amine ligands on copper leaching from copper amine treated samples. (———) 1.0% copper treated; (·········) 0.5% copper treated

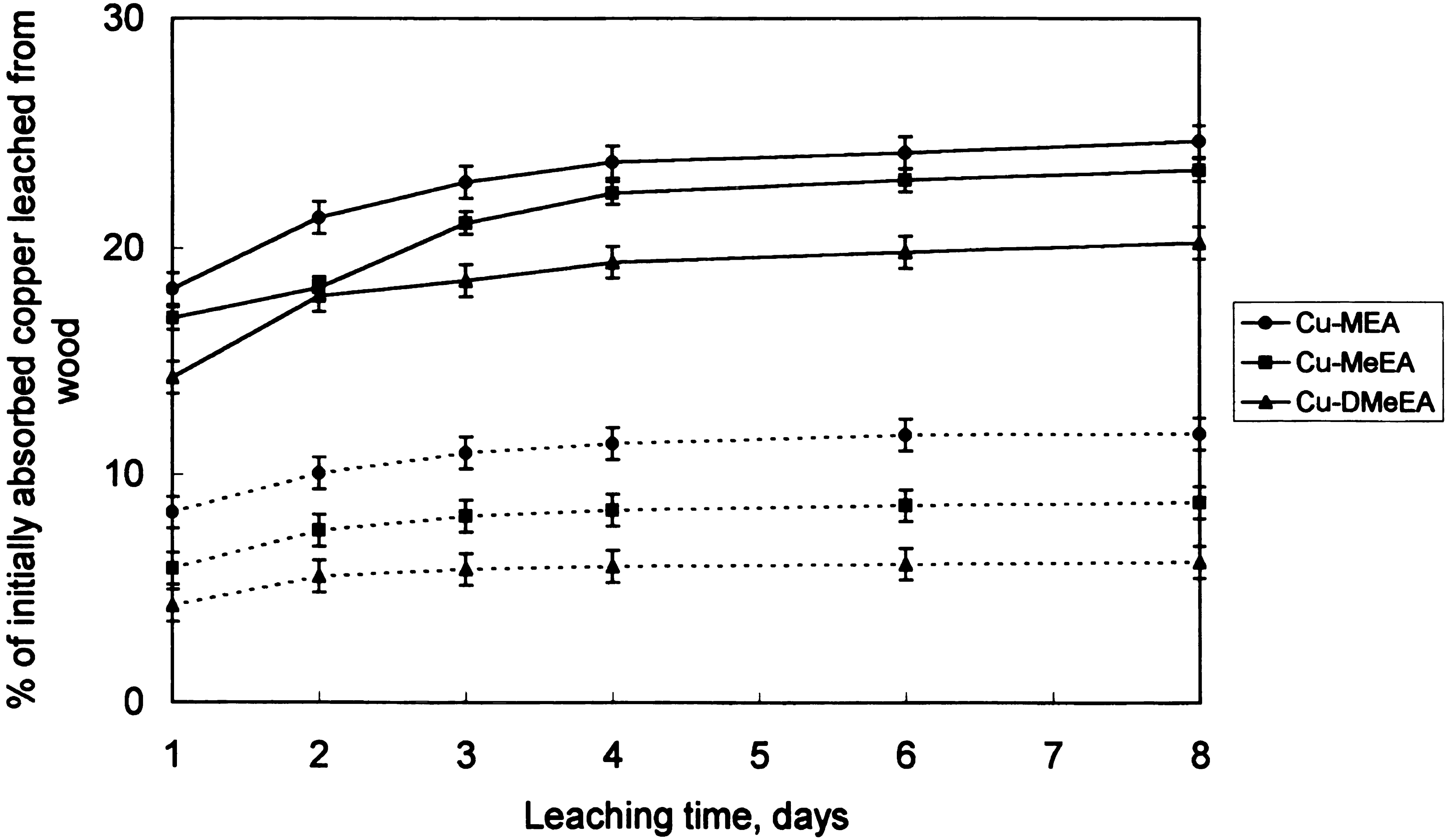

30
20
10
0
% of initially absorbed copper leached from wood
1
2
3
4
5
6
7
8
Leaching time, days
Cu-MEA
Cu-MeEA
Cu-DMeEA

Figure 2.4

copper increases. Tertiary amine DMeEA system exhibits a minimum percentage of copper loss, while primary amine MEA formulation treated samples lose more copper. After an 8-day water leaching of the cubes treated with 0.5% copper solution, about 5% of the absorbed copper leached into solution for the tertiary amine DMeEA system, 8% for secondary amine MeEA and 12% for primary amine MEA.

2.4.3 Effect of Amine to Copper Molar Ratios

Increasing amine to copper molar ratio improves the stability of copper amine complex (Hancock 1981), and hence increases the penetration and retention of the copper amine complex in wood. Change in the molar ratio of amine to copper can alter the copper absorption and leaching resistance. Figure 2.5 represents the copper absorption in wood pressure-treated with copper amine solutions with amine to copper molar ratios varying from 3 to 8. The molar ratio of amine to copper affects copper absorption greatly in Cu-MeEA and Cu-DMeEA formulation systems. At amine to copper molar ratios below 4, the retention of copper in wood increases rapidly as the molar ratio increases, and then copper absorption tends to saturate as the amine to copper molar ratio further increases. The influence of amine to copper molar ratio is not so pronounced in the Cu-MEA system as in the Cu-DMeEA and Cu-MeEA formulations. Increase in amine to copper molar ratio from 3 to 8 in Cu-MEA formulation only causes a slight increase of copper absorbed in wood. Increased copper absorption may be due to easier diffusion of copper in wood with the increase in amine content.

Figure 2.6 displays the percentage of copper loss after 8-day water leaching at different amine to copper molar ratios. Higher molar ratio accelerates copper loss during leaching. The percentage of copper loss is approximately proportional to the molar ratio

Figure 2.5 Effect of amine to copper molar ratios on copper retention. Copper amine solutions were made by mixing copper hydroxide with amines at different ratios. (——) 1.0% copper treated; (┄┄) 0.5% copper treated

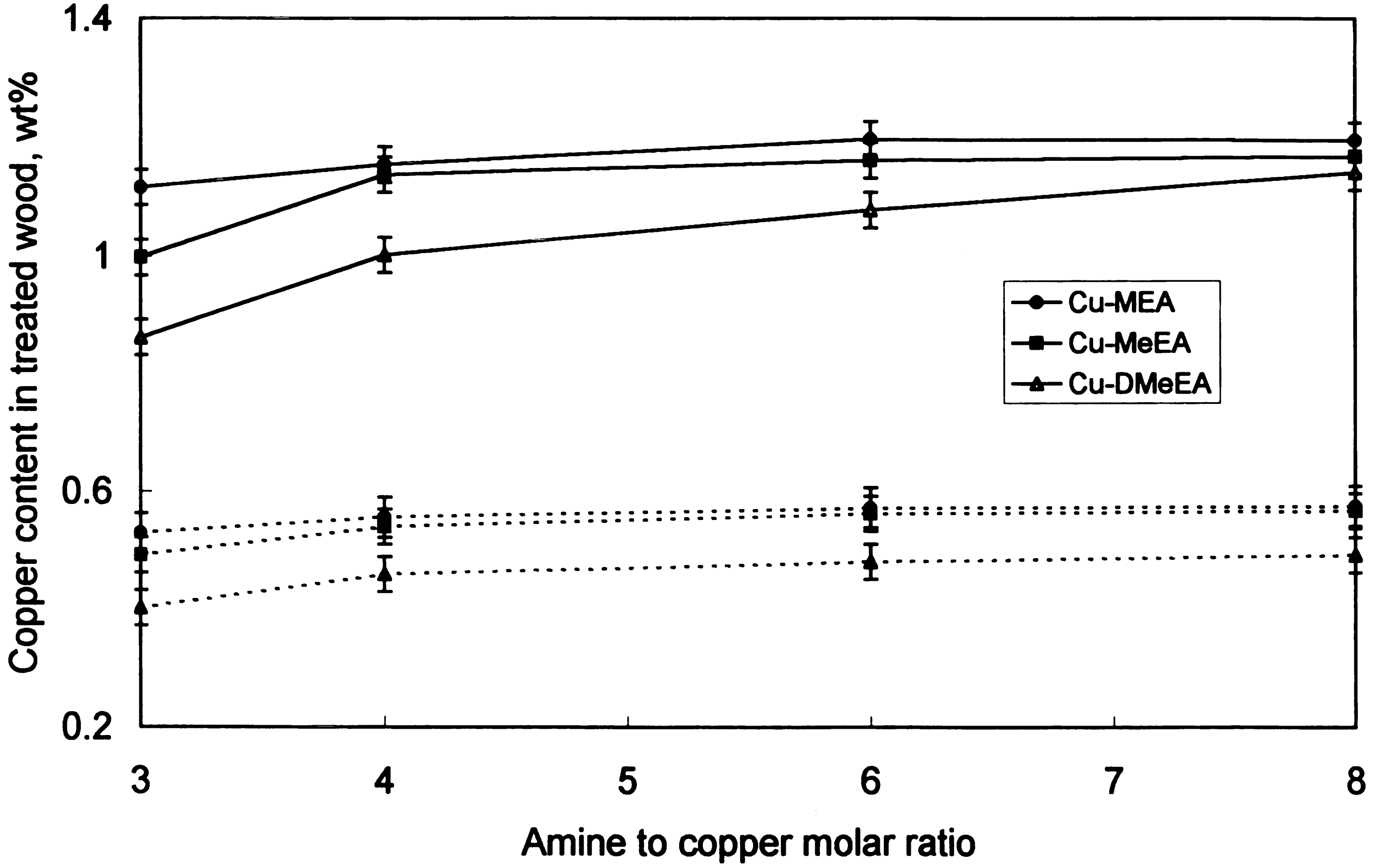

1.4
1
0.6
0.2
Copper content in treated wood, wt%
3
4
5
6
7
8
Amine to copper molar ratio
Cu-MEA
Cu-MeEA
Cu-DMeEA

Figure 2.5

Figure 2.6 Effect of amine to copper molar ratios on copper leaching from copper amine treated samples. (——) 1.0% copper treated; (·······) 0.5% copper treated

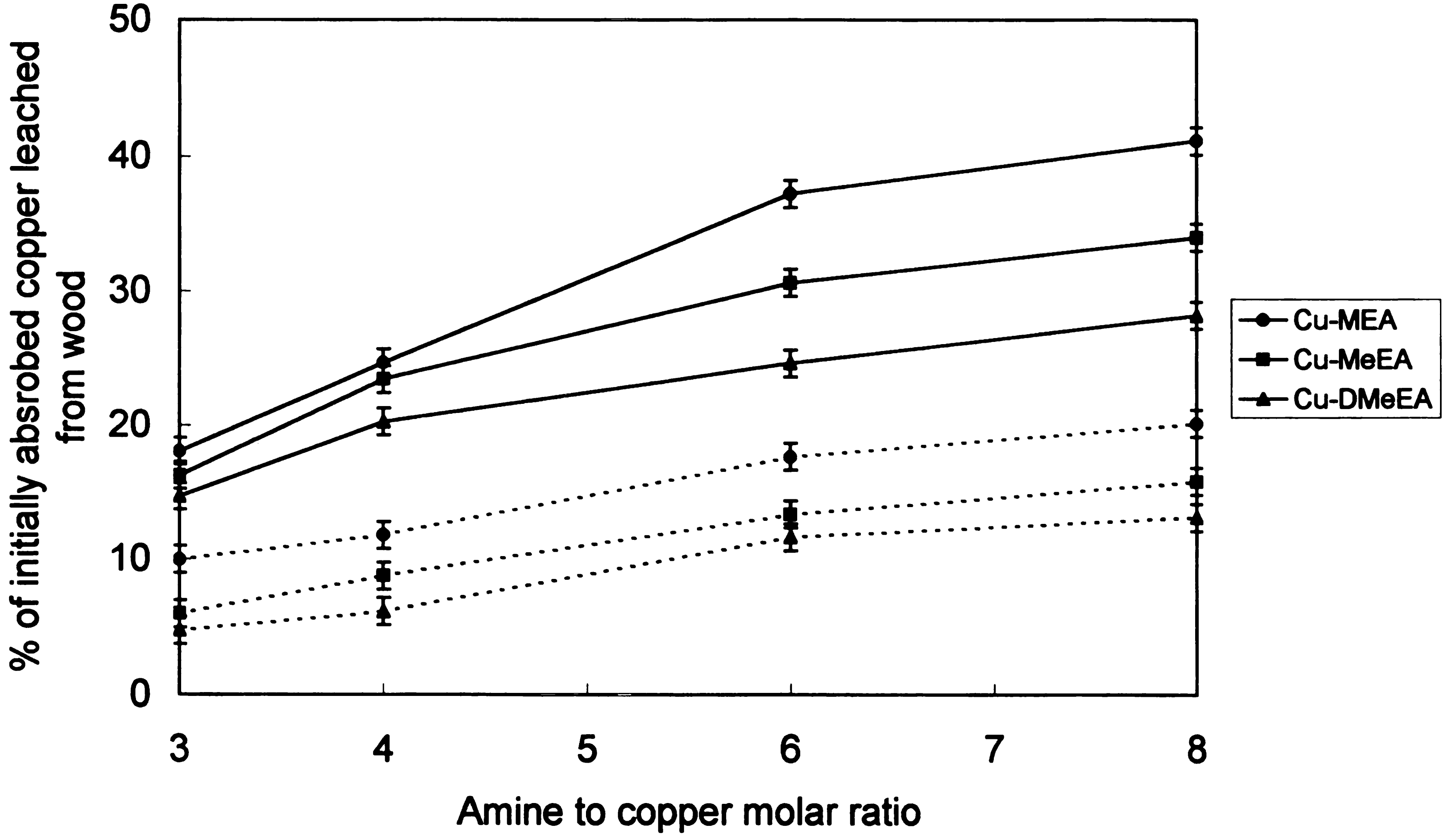

% of initially absrobed copper leached from wood
50
40
30
20
10
0
3
4
5
6
7
8
Amine to copper molar ratio
Cu-MEA
Cu-MeEA
Cu-DMeEA

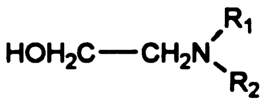
Figure 2.6

of ligand to copper for all the formulations. This suggests that an increase in the amine to copper molar ratio reduces the ability of copper to fix in wood, and therefore increases the leaching of copper in treated samples.

2.4.4 Copper Fixation Mechanism

Cupric ions form a 5-member ring complex with ethanolamine through amino and hydroxyl groups in aqueous solution as proposed in Figure 2.7. Previous study showed that the number of ligand molecules to one cupric metal ion was two at both low and high ligand-to-metal ratios (Casassas *et al.*, 1989). As solution pH increases, deprotonation of hydroxyl groups occurs. At neutral or low basic conditions, only one proton from hydroxyl groups of the amine ligand is released (Figure 2.7). As the pH further increases, another proton from hydroxyl groups of the amine ligand is released and the complex becomes a non-conducting species with no charge (Figure 2.7C). Deprotonation enhances the stability of the copper amine complex (Jensen, 1971; Hancock, 1981; Hancock and Nakani, 1984 and Casaccas *et al.*, 1989). The three species of copper amine complex maintain a dynamic equilibrium in aqueous solution and the proportion of these species varies with the pH of the solution. According to Tauler and Casassas (1986), complex B is the main species when the pH of the solution is around 8.5, and complex C becomes dominant when the pH is above 10.

When wood is pressure treated with copper amine solutions, the copper amine complexes penetrate into the wood substrate. The penetration of copper into wood is related to the stability of the copper amine complexes. A stable complex should result in a deep penetration of the complex and higher absorption of copper. A less stable copper

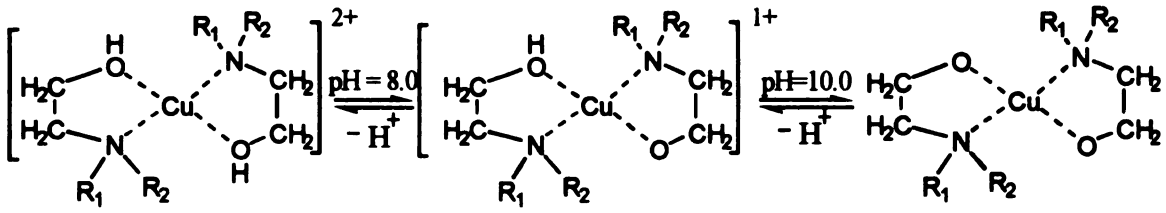


$HOH_2C—CH_2N(R_1)(R_2)$

Monoethanolamine: $R_1 = R_2 = H$

2-Methylamino-ethanol: $R_1=H$, $R_2 = CH_3$

N, N-dimethyl-ethanolamine: $R_1 = R_2 = CH_3$



A B .C

Figure 2.7 Top: Amine ligands. Bottom: Copper amine complexes amine complex tends to react with wood readily. The reaction is a neutralization of anionic groups. This may lower the swelling at the wood surface and retard the penetration of additional treating solution.

If the copper amine complex exists in wood by physical interaction, it will be leached out easily by water. To be fixed in the wood cell wall, the copper amine complexes interact with wood through chemical reactions. Wood is a weak acidic substrate, in which functional groups, such as carboxylic groups and phenolic hydroxyl groups, are active sites for interactions with copper. Two types of reaction mechanisms, namely, ligand exchange and complexation, are proposed here.

In the ligand exchange reaction mechanism, copper amine complexes exchange ligands with wood and release one amine molecule (Figure 2.8A). This ligand exchange mechanism is proposed because of the presence of the non-conducting species of copper amine complexes (Figure 2.7C). This assumption was previously proposed by Kamdem *et al.* (1996) and Thomason and Pasek (1997). In the second possible reaction mechanism, non-charged species of copper amine complexes are transformed into charged species during the treatment of wood. Functional groups, such as wood-COOH and wood-phenolic, can complex with the charged species to form a stable wood-copper amine complex (Figure 2.8B).

These reactions are influenced by the stability and the pH values of copper amine complexes. For the ligand exchange reaction, the less stable the copper amine complex, the easier the complex disassociation will be, and therefore the reaction with wood will be driven forward. For the complexation mechanism, the lower the pH of the treating

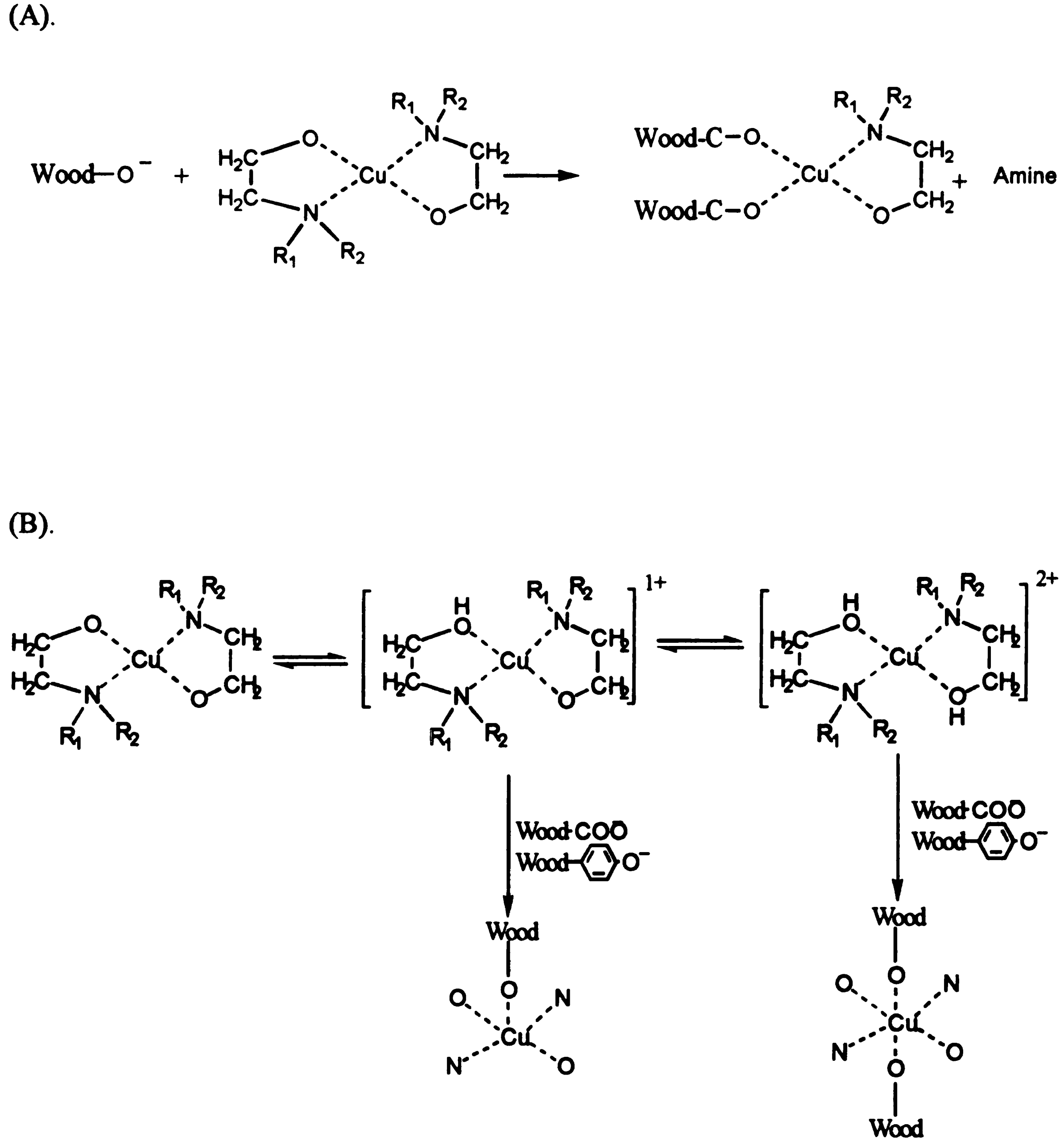


Figure 2.8 Copper amine –wood interactions
A). Ligand exchange and B). Complexation

solutions, the more charged species of complex (Figure 2.7A and 2.7B) will be present, and hence the interaction between wood and complex will be more likely.

The pH of treating solution varies with the copper source (Table 2.1) and amine concentration (Table 2.2). As mentioned above, the higher the pH of the treating solution, the more stable the copper amine complex is. The complexes from copper hydroxide and copper carbonate system are more stable than those from copper sulfate and copper nitrate. As a result, high retentions of copper were obtained from copper hydroxide and copper carbonate. However, a stable complex resulting from high pH will not promote a good interaction between copper and wood according to the above reaction mechanisms. This explains the low copper loss from copper sulfate and copper nitrate formulations.

The stability of the complex is also influenced by the amine ligand and the amine to copper molar ratio. The copper complex of primary amine is more stable than those of secondary amine and tertiary amine due to the steric hindrance of methyl groups. Hancock and Nakani (1984) pointed out that the steric effect outweighed the inductive effect when copper ion (Cu^{2+}) formed complex with amine ligands. The high stability of copper complex with primary amine or with high amine to copper molar ratio will lead to good penetration of the complex in wood and hence increase the retention of copper. Due to its low stability, copper DMeEA complex is easier to react with wood than copper MEA. This explains lower copper loss from DMeEA system, and high copper loss from copper MEA during laboratory leaching test. Increasing the molar ratio of amine to copper enhances the stability of complex and increases the pH of treating solution (Table 2.2), and therefore improves the penetration of complexes. At higher molar ratio, copper amine complexes tend to exist as non-charged species and may block the ligand exchange

Table 2.2 pH of copper amine treating solutions containing 0.5% copper from copper hydroxide and different amine ligands

Amine Ligands	Amine to copper molar ratio			
	3	4	6	8
MEA	10.6	10.8	11.1	11.2
MeEA	10.7	10.8	11.2	11.3
DMeEA	10.5	10.6	11.0	11.1

reaction and complexation reaction, and therefore block the interactions of wood functional groups with the copper amine complexes. This accounts for lower leaching resistance when the molar ratio of amine to copper increases.

2.5 Conclusions

The copper retention and leaching of Cu-EA treated wood were influenced by the copper amine formulations. High pH formulation system resulted in higher copper retention in wood, but lower copper leaching resistance. Increase in the molar ratio of amine to copper improved copper penetration into the wood, and therefore increased the copper retention. However, high amine to copper ratio caused high copper loss during water leaching. As a general rule, in formulating a copper amine treating solution, a balanced pH, amine ligand, and amine to metal ratio should be taken into consideration to improve copper retention while minimizing the copper loss during leaching. The biological impact of these parameters needs to be investigated.

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Chapter 3

Effect of Wood Composition on Copper Absorption

3.1 Abstract

The effect of individual wood components on copper absorption when treated with copper amine solution was investigated. Data showed that the copper absorption by wood substrates experiences a rapid increase at the first 30 minutes and then reaches a plateau. Lignin and xylan exhibit high copper absorption, suggesting that hemicellulose and lignin in wood play a significant role in bonding copper, while the role of cellulose in retaining copper is negligible. Removal of extractives from wood also decreases the amount of copper absorbed.

3.2 Introduction

Wood contains three major constituents: cellulose, hemicellulose, and lignin. In addition, a small percent of extractives is also present. These wood components play an important, but poorly understood, role in absorbing copper when wood is exposed to copper based preservatives. Early study by Belford and Preston (1957) indicated that cellulose in wood reacted with copper preservative to form metallo-cellulose complexes when wood was impregnated with aqueous solutions of copper sulfate and copper sulfate-potassium dichromate mixtures. By conducting a study of copper amine reaction with wood, Thomason and Pasek concluded that hemicellulose was the major wood constituent for selective absorbing copper. Pizzi (1982) and Xie *et al.* (1995), who examined the interaction between copper and lignin on the basis of lignin model compounds, proposed that lignin was responsible for fixing copper by forming copper-lignin complex.

In this experiment, copper amine preservatives were used to treat different wood components and model compounds. The effect of the various functional groups on copper absorption was studied.

3.3 Materials and Methods

3.3.1 Materials

In this study, unextracted and extracted Southern pine (SP) sapwood, cellulose, lignin, holocellulose and a hemicellulose model compound, xylan, were used. Extractive free wood samples were obtained by extracting SP with ethanol/toluene. Cellulose, organosolv lignin and xylan were purchased form Aldrich Chemical Co.

Holocellulose was prepared by delignification of wood with acidified sodium chlorite using modified methods reported by Ona *et al.* (1995). 20 grams of extractive-free wood powder and 300ml 6% sodium chlorite were added to a 500ml flask, followed by addition of 6ml glacial acetic acid (pH4.0). The mixture was heated to 70°C on a water bath. The flask was continuously stirred for 30 minutes, and then another 2 grams of sodium chlorite and 1ml glacial acetic acid were added to the flask. After 60 minutes, the mixture was filtrated with a glass-filtering crucible and washed with cold distilled water and acetone. The residue was dried under a high vacuum and holocellulose resulted.

Copper monoethanolamine (Cu-EA) treating solutions were made by dissolving copper hydroxide in aqueous monoethanolamine with the molar ratio of amine to copper of 4. The copper concentrations in the treating solutions were 0.5 and 1.0% by weight, respectively.

3.3.2 Treatment

About 2.5 grams wood substrates were treated with 50 grams of 0.5 and 1.0 wt % Cu-EA treating solutions in a 100ml flask, sealed and agitated on a wrist-shaker for 0.2, 0.5, 2, 4, 8, 24 hours. After the agitation, samples were filtered through glass fiber filters and washed continuously with deionized water until the conductivity of the eluent water was constant. The objective of continuous washing with deionized water was to minimize physical absorption of copper in treated sample. The treated and water-washed samples were air-dried for two weeks and analyzed by atomic absorption spectrometry (AAS) to determine copper content.

3.3.3 Analysis of Phenolic Hydroxyl Groups

The procedure used in this research was a slightly modified method previously described by Francis *et al.* (1991). Approximate 100mg lignin or 200mg wood sawdust in a 20 ml glass centrifuge tube was treated with 6ml sodium periodate solution (75 mg/ml), to which 1mL of distilled water containing 3 mg acetonitrile was added as an internal standard. Both solutions were cooled to 4°C prior to addition to the sample. The suspension was homogenized and kept in the dark at 4°C in a refrigerator with occasional stirring.

The mixture was centrifuged to obtain a clear solution for GC analysis. Methanol and the internal standard (acetonitrile) were determined with a 1.8-m x 0.32-cm stainless steel column packed with Tenax GC. The GC was operated at 80°C with an injection-port temperature of 150°C and a detector temperature of 250°C. a nitrogen flow of 60mL/min was maintained.

3.4 Results and Discussion

When wood substrates were exposed to copper-amine treating solution, copper absorption by wood substrates except cellulose exhibited a rapid increase within the first 30 minutes (Figure 3.1 and 3.2). After about 4 hours of exposure, copper absorption tended to level off. This fast copper absorption during initial stages has also been reported in other copper-based wood preservative systems, such as CCA (Cooper, 1991; Dahlgren, 1972). The copper absorbed by cellulose did not noticeably change as exposure time and copper concentration in treating solution increased.

Table 3.1and 3.2 illustrate the copper absorption on different wood substrates. Significant copper absorption difference is exhibited among the different wood substrates. Lignin was the most active material, retaining significantly higher level of copper than the other wood substrates. This organosolv lignin is expected to contain about 4 times as much phenolic hydroxyl groups as the native lignin in softwood or hardwood. In contrast, cellulose was the least reactive site for copper among the wood substrates. Holocellulose, which consists of cellulose and hemicellulose, showed a relatively higher copper absorption, suggesting that hemicellulose possesses higher copper affinity. As a model compound of hemicellulose, xylan displays higher copper reactivity than holocellulose. The role of wood extractives in copper absorption cannot be neglected. When the extractives were removed from wood, the extractive-free wood showed less copper absorption than unextracted wood (Figure 3.1 and 3.2).

Figure 3.1 Effect of wood components and exposure time on copper absorption from 0.5% copper amine treating solution

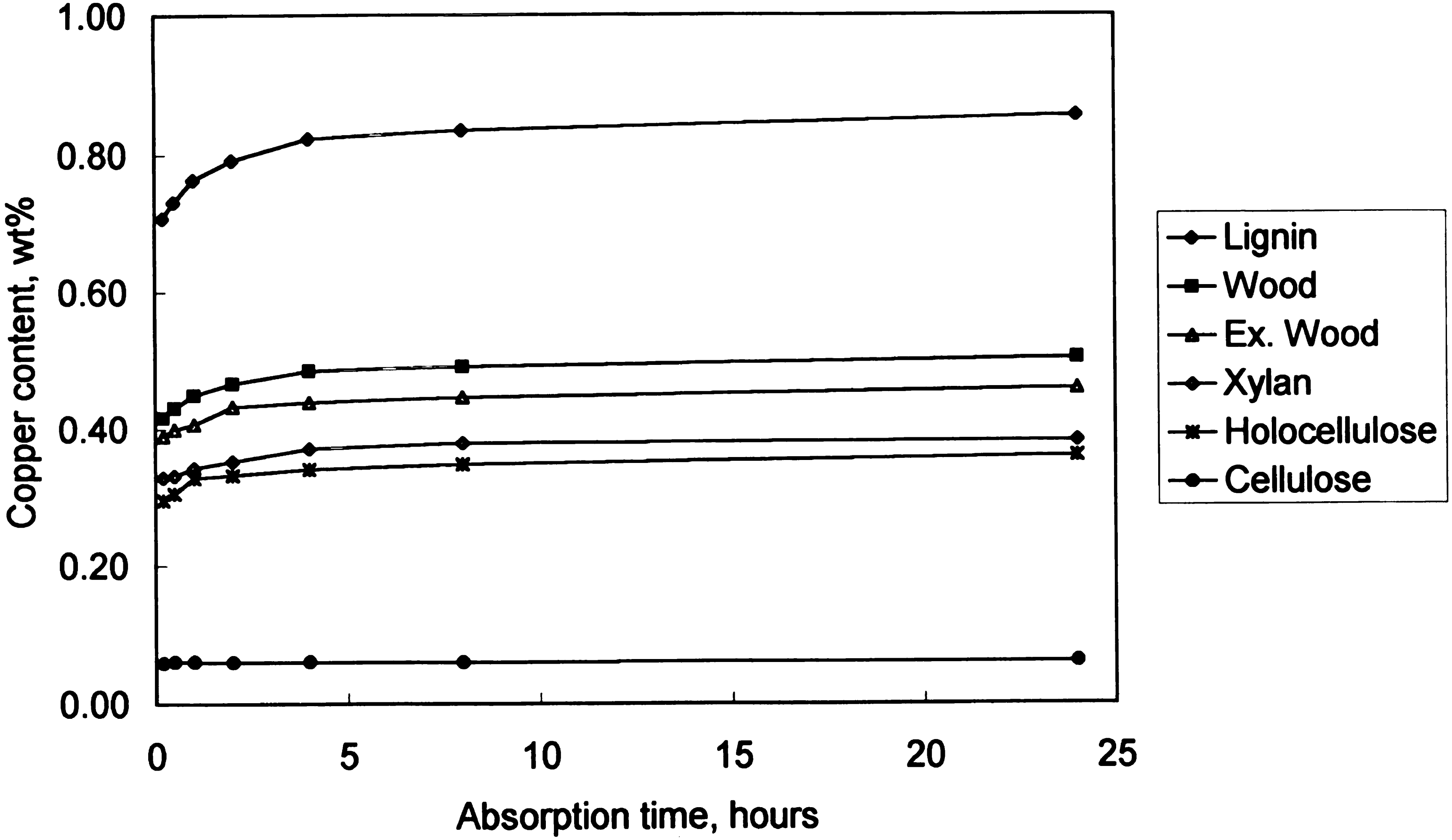
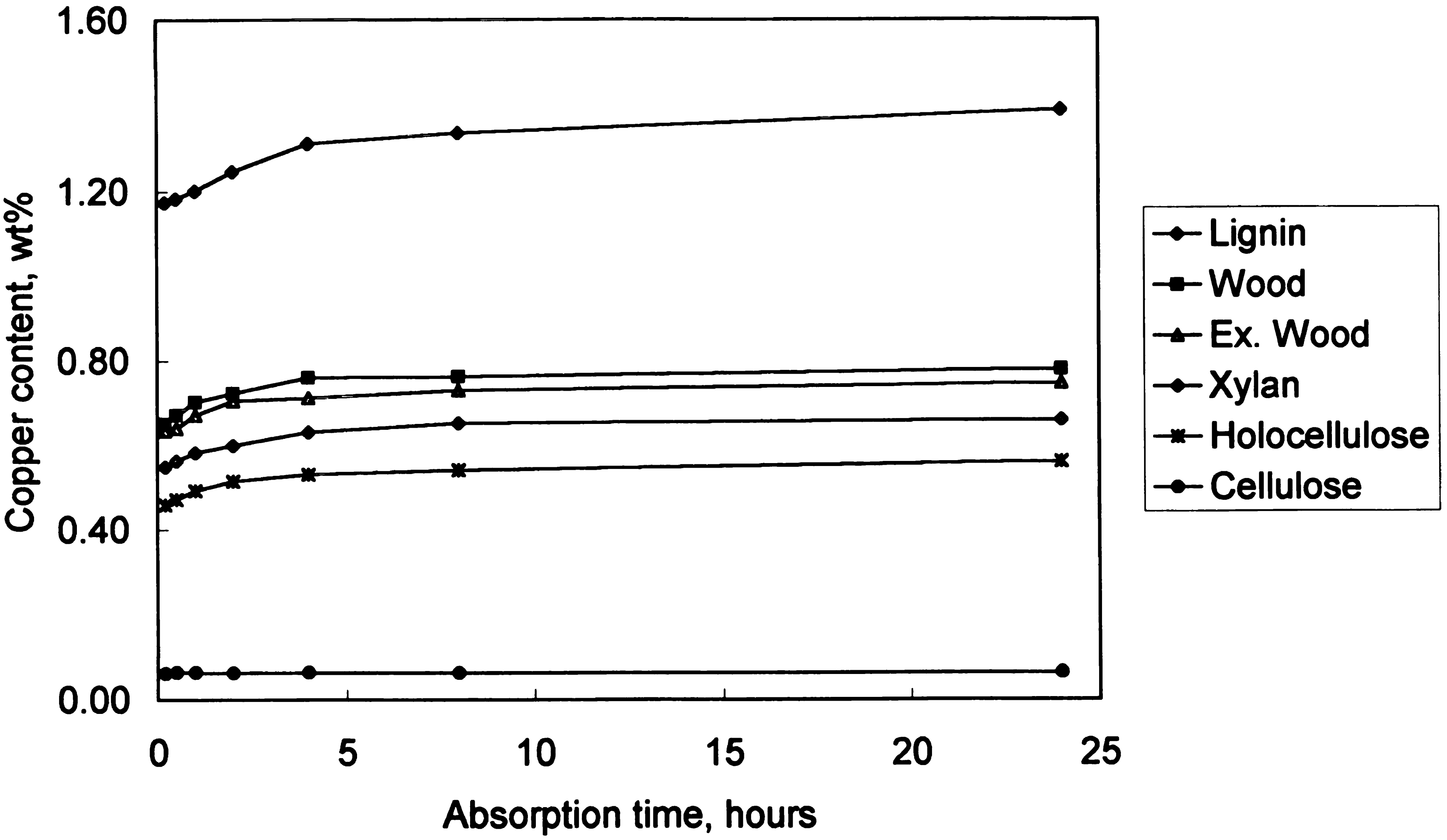

1.00
0.80
0.60
0.40
0.20
0.00
Copper content, wt%
0
5
10
15
20
25
Absorption time, hours
Lignin
Wood
Ex. Wood
Xylan
Holocellulose
Cellulose

Figure 3.1

Figure 3.2 Effect of wood components and exposure time on copper absorption from 1.0 % copper amine treating solution



1.60
1.20
0.80
0.40
0.00
Copper content, wt%
0
5
10
15
20
25
Absorption time, hours
Lignin
Wood
Ex. Wood
Xylan
Holocellulose
Cellulose

Figure 3.2

Table 3.1 Copper absorption in wood substrates treated with 0.5 wt % copper amine solution

Time Hours	Lignin	Wood	Ex. Wood	Xylan wt % copper	Holocellulose	Cellulose
0.2	0.708	0.416	0.389	0.329	0.296	0.0589
0.5	0.731	0.430	0.399	0.331	0.305	0.0603
1.0	0.763	0.449	0.407	0.342	0.328	0.0604
2.0	0.792	0.466	0.432	0.352	0.332	0.0597
4.0	0.823	0.484	0.439	0.370	0.341	0.0609
8.0	0.836	0.492	0.446	0.379	0.348	0.0600
24.0	0.855	0.503	0.459	0.383	0.360	0.0610

Table 3.2 Copper absorption in wood substrates treated with 1.0 wt % copper amine solution

Time Hours	Lignin	Wood	Ex. Wood	Xylan	Holocellulose	Cellulose
				wt % copper		
0.2	1.174	0.650	0.634	0.549	0.458	0.0618
0.5	1.183	0.671	0.640	0.563	0.472	0.0633
1.0	1.201	0.702	0.671	0.582	0.493	0.0634
2.0	1.247	0.723	0.705	0.599	0.515	0.0627
4.0	1.312	0.760	0.711	0.631	0.530	0.0639
8.0	1.336	0.762	0.729	0.651	0.541	0.0630
24.0	1.390	0.779	0.747	0.659	0.560	0.0640

The lower copper absorption on cellulose may be due to the limited accessibility of the cellulose molecules and lower reactivity of aliphatic hydroxyl groups in cellulose molecules. Cellulose chains have many primary and secondary hydroxyl groups and these hydroxyl groups form intra- and inter-molecular hydrogen bondings within and among cellulose chains. These hydrogen bondings are arranged regularly, which results in a crystalline system of cellulose. The crystalline properties of cellulose limit the accessibility of reactants into cellulose. Moreover, the aliphatic hydroxyl group is very difficult to be ionized in aqueous solution, which makes it less likely to fix copper chemically. The small amount of copper absorbed by cellulose may be due to the secondary forces, such as dipole-dipole and Van der Waals attractions, in amorphous portion of cellulose.

Although hemicellulose in wood contains a great deal of aliphatic hydroxyl groups, it contributes most of the carboxylic groups in wood, which tend to be very reactive with copper. For instance, uronic acid groups in hemicellulose have been proven to be active for copper absorption (Rennie *et al.*, 1987). This explains why holocellulose and xylan absorbed more copper than cellulose. Since xylan possesses higher ratio of carboxylic acids than holocellulose, more copper was absorbed in xylan than in holocellulose (Figure 3.1 and 3.2).

Previous study by Bland (1963) indicated that, when wood was treated with copper solution, copper was concentrated in the compound middle lamella, showing that lignin is also responsible for the copper absorption. Lignin has been reported as a primary reaction site for copper in alkaline solutions (Pizzi, 1982, Lebow and Morrell, 1995). The high reactivity of lignin has been attributed to the phenolic hydroxyl (PhOH) groups in lignin. A study by Sjöström (1989) demonstrated that phenolic hydroxyl groups were ionized in alkaline conditions (pH 10-12) and these hydroxyls can react with copper ion. The very high copper absorption by lignin in this study is due to the highly phenolic nature of lignin. Aldrich Chemical Co. confirmed that the lignin was extracted from a mixture of hardwoods (birch, maple and poplar with 35: 50:15 by weight). This mixture is the standard used in the research and development for the ALCELL Process (Goyal *et al.*, 1992). A mildly acidic ethanol / water mixture is used to hydrolyze some inter-unitary ether bonds in the lignin (Goyal *et al.*, 1992; Gallagher *et al.*, 1989). This depolymerizes the lignin and increases its phenolic hydroxyl content and its solubility in ethanol/water. The GC analysis showed that the organosolv lignin and the Southern pine used in this study had 64 PhOH/100 C9 units and 12.9 PhOH/100 C9 units, respectively. A value of 47 PhOH/100 C9 units have been reported for the dissolved or extracted lignin from the ALCELL Process (Gallagher *et al.*, 1989). Once the ethanol is evaporated, this lignin precipitates out of the acidic aqueous solution. Native softwood lignin contains approximately 12 PhOH/100 C9 units and the value is normally smaller for native hardwood lignin (Francis *et al.*, 1991).

Although only small percentage of extractives exists in wood, the role of extractives in bonding copper is important (Figure 3.1 and 3.2). Wood extractives have a certain amount of phenolic hydroxyl groups and carboxylic acid groups (Fengel and Wegener, 1984). These groups cause copper absorption between wood and extractive-free wood treatment to differ.

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Chapter 4

Investigation of Copper Bonding Sites by Fourier Transform Infrared Spectroscopic Analysis

4.1 Abstract

The interactions of copper monoethanolamine (Cu-MEA) and wood components were studied by using Fourier transform infrared spectroscopy (FTIR). In Cu-MEA treated wood, significant reduction was noticed on the band attributed to carbonyl vibration from carboxylic groups at 1735±5 cm^{-1} and an increase in band intensity was obtained from carbonyl in carboxylate at 1595±5 cm^{-1}. The same observation was made in Cu-MEA treated holocellulose. The FTIR spectrum of cellulose did not change after Cu-MEA treatment. When the carboxylic acid groups were introduced into cellulose by oxidation, Cu-MEA treatment of oxidized cellulose resulted in the disappearance of the carboxylic acid band, which further confirmed that carboxylic groups were active bonding sites for copper. Cu-MEA treated lignin resulted in a reduction in the aromatic ester band at 1710±5 cm^{-1} and an increase in carbonyl from carboxylate at 1595±5 cm^{-1}. Bands at 1370 cm^{-1} and 1221 cm^{-1}, assigned to phenolic hydroxyl groups, exhibited a decrease in intensity after the treatment. From these data, it is concluded that Cu-MEA interacts with carboxylic groups, phenolic hydroxyl groups and ester groups from lignin to form copper carboxylate and phenolate complexes.

4.2 Introduction

Copper-based preservatives are widely used in wood protection due to the excellent fungicidal activity of copper. The interactions of copper-based wood preservatives with wood and the bonding sites for copper have long been an active wood preservation research area. As a result, a lot of hypotheses have been proposed. Pizzi (1982) concluded that copper was physically absorbed by studying the reactions of chromate copper arsenate (CCA) with cellulose, glucose, guaiacol and finely group pine sapwood. Ion exchange reactions with wood have been postulated since wood contains weak acid groups that are able to form complexes with copper cation (Dahlgren, 1972; Pizzi, 1982). Cooper (1991) conducted extensive research on cation exchange adsorption of copper on wood, confirming that wood is a weak acid cation exchange material. At low pH value, uronic acid groups in hemicellulose were reported to be the primary sites for ion exchange (Rennie *et al.*, 1987; Copper, 1991), while lignin became increasingly important exchange sites at higher pH (Pizzi, 1982). Functional groups in wood, such as aliphatic hydroxyl group, phenolic hydroxyl group and carboxylic group, have been proposed as the potential bonding sites for copper. Research by Lebow and Morrell (1993) demonstrated that the phenolic group in wood provided reactive sites for copper. Carboxylic groups in wood have been reported as the bonding sites for copper (Craciun and Kamdem, 1997; Thomason and Pasek, 1997).

Apart from all these investigations, spectroscopic analysis has also been employed to obtain information about the chemical interactions between wood components and preservatives. Fourier transform infrared spectroscopy is commonly used to examine functional groups and components in wood sample (Ostmeyer *et al.*, 1989). The technique has also been used to identify and qualify major wood components such as lignin, cellulose, glucose and their modified derivatives (Michell, 1995; Rodrigues *et al.*, 1998).

In the previous experiment, the role of individual wood components in copper absorption was investigated. In this experiment, diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) was used to monitor the change in the spectra of wood components after treatment with copper amine preservative, examine the interactions of this preservative with various functional groups in wood and investigate the bonding sites of copper in wood.

4.3 Materials and Methods

4.3.1 Materials

Kiln-dried southern pine (SP) sapwood was used for the current study. SP was extracted with ethanol/toluene and then ground into sawdust to pass 60 mesh. Holocellulose was prepared by delignification of wood with acidified sodium chlorite using modified methods reported by Ona *et al.* (1995). Cellulose and organosolv lignin were purchased form Aldrich Chemical Co. Copper monoethanolamine (Cu-MEA) treating solution was made by dissolving copper hydroxide in aqueous MEA with the molar ratio of amine to copper of 4.

4.3.2 Oxidation of Cellulose

Cellulose was first oxidized to oxycellulose by sodium metaperiodate, and the aldehyde group in oxycellulose was then oxidized to carboxylic group by chlorous acid (Figure 4.1).

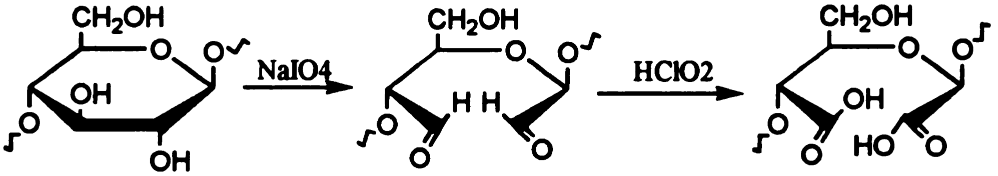

Figure 4.1 Oxidation of cellulose into oxidized cellulose

4.3.3 Treatment

About 2.5 grams wood substrates were treated with 50 grams of Cu-MEA treating solution containing 1.0% copper by weight in 100ml flasks. The flasks were sealed and agitated on a wrist-shaker for 24 hours. After the agitation, samples were filtered through glass fiber filters and washed continuously with deionized water until the conductivity of the eluent water was constant. The purpose of continuous washing with water was to minimize physical absorption of copper in treated samples. The treated and water-washed samples were air-dried for two weeks and analyzed by FTIR analyses.

4.3.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analyses were performed on a Nicolet Protégé 460 spectrometer equipped with Spectra-Tech diffuse reflectance accessory. Potassium bromide (KBr) was used to collect background. Air-dried samples were mixed with KBr before spectrum collection. All spectra were collected using diffuse reflectance Fourier transform infrared spectroscopic technique (DRIFT). Spectra were acquired for a total of 64 scans on a 400 to 4000 cm^{-1} wavenumber range with a resolution of 4 cm^{-1}. All spectra were displayed in absorbance and limited to 600-1800 cm^{-1} region.

4.4 Results and Discussion

The interest region of all spectra is limited to 600-1800 cm^{-1}. Figure 4.2 shows the FTIR spectra of wood and Cu-MEA treated wood. The dotted line denotes the spectrum of Cu-MEA treated wood. Major band assignments in the infrared spectra, listed in Table 4.1, were made according to those of Sarkanen *et al.*(1967a, b), Michell *et al.* (1965), Liang and Marchessault (1959), and Tolvaj and Faix (1995). The band at 1739 cm^{-1} in

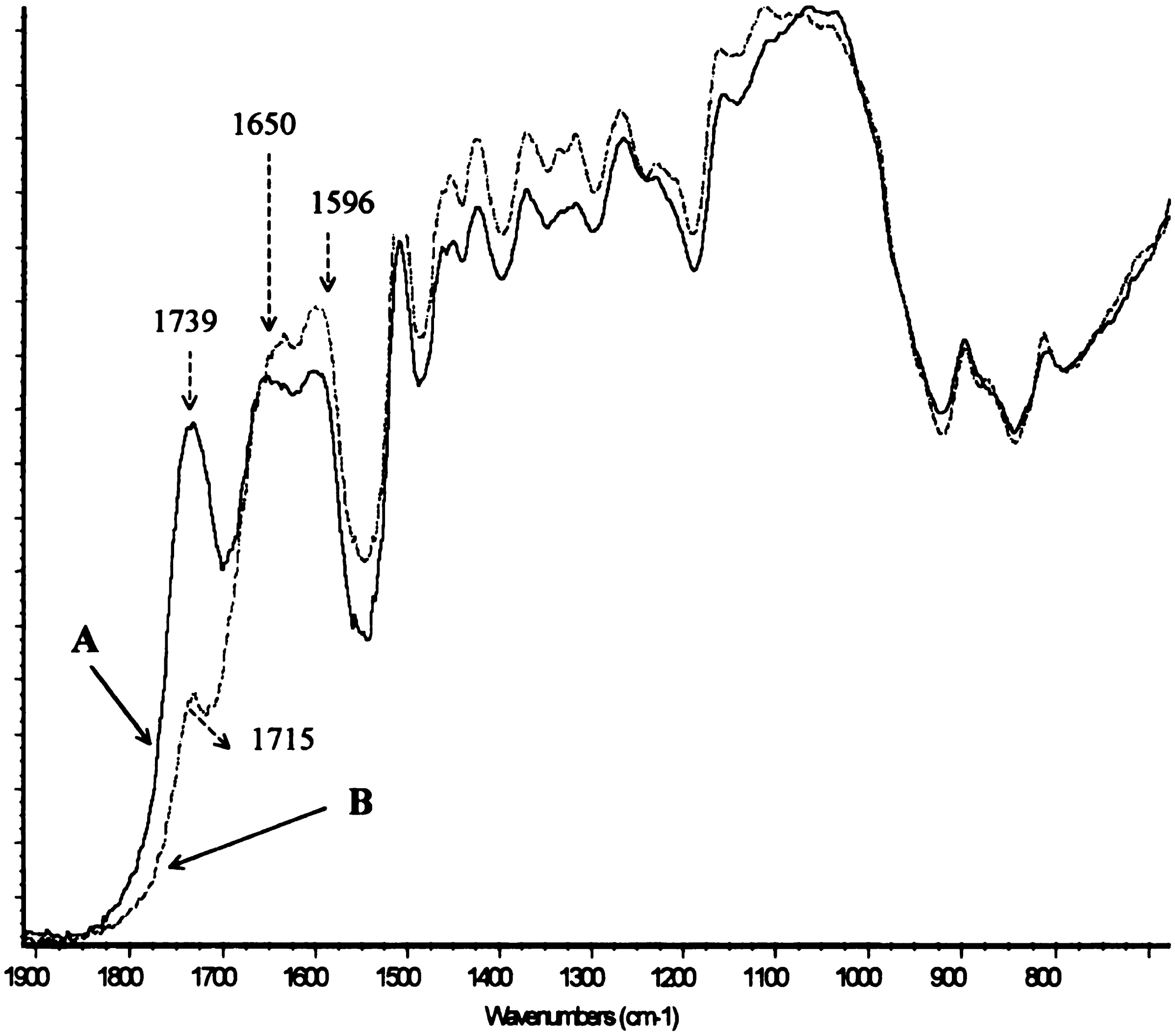

Figure 4.2 FTIR spectra of (A). Wood and (B). Cu-MEA treated wood

Table 4.1 Assignments of infrared absorption bands in wood.

Position in cm^{-1}	Band Assignments
1739	C=O stretching in COOH
1651	C=O stretching of α-keto groups
1595	Aromatic skeletal vibrations
1510	Aromatic skeletal vibrations
1470	C-H deformations (asymmetric)
1425	Aromatic skeletal vibrations
1370	C-H deformations (symmetric)
1265	C-O-C asymmetric stretching vibration of aryl ether linkages
1230	C-O-C asymmetric stretching vibration of aryl-alkyl ether linkages
1150, 1063	C-O deformation

Figure 4.2A was assigned to carboxyl stretching vibration in carboxylic acid (Tolvaj and Faix, 1995; Michell *et al.*, 1965). After treatment, this band diminished and a weak band at 1715 cm^{-1} was left as a shoulder. The intensity of the band at 1596 cm^{-1}, relative to the band at 1650 cm^{-1}, was enhanced in Cu-MEA treated wood. The subtraction of spectrum of untreated wood from that of Cu-MEA treated wood is illustrated in Figure 4.3. The subtraction result confirmed that the intensity decreased at 1739 cm^{-1} and the intensity increased at 1596 cm^{-1}. The disappearance of the band at 1739 cm^{-1} in treated wood can be attributed to the dissociation of carboxylic acid into carboxylate anion and further interaction with copper amine complex (Nakamoto, 1978). The increase of the band intensity at 1596 cm^{-1} is due to carbonyl stretching vibration in carboxylate salt. It has been widely reported that the carboxylic band at around 1735 cm^{-1} shifted to 1590 cm^{-1} upon conversion to a carboxylate (Hergert, 1971). The weak band at 1715 cm^{-1} in Cu-MEA treated wood may be due to carbonyl stretching from ß-ketone groups in lignin (Michell, 1965). All the information suggests that the carboxylic acid groups are very active sites for complexing copper. Due to the intrinsic complexity of the structure of wood, it is difficult to interpret the spectra in other regions.

To elucidate the interactions of Cu-MEA with wood, individual wood components, such as cellulose, holocellulose and lignin, were treated with Cu-MEA and their spectra were shown in Figure 4.4- 4.7. Figure 4.4 shows the spectra of cellulose and Cu-MEA treated cellulose. There is no noticeable change in FTIR spectrum of cellulose after being treated with Cu-MEA. Absorption test showed that only a minimal amount of copper (Table 3.2) was absorbed by cellulose when cellulose was treated with 1.0% Cu-

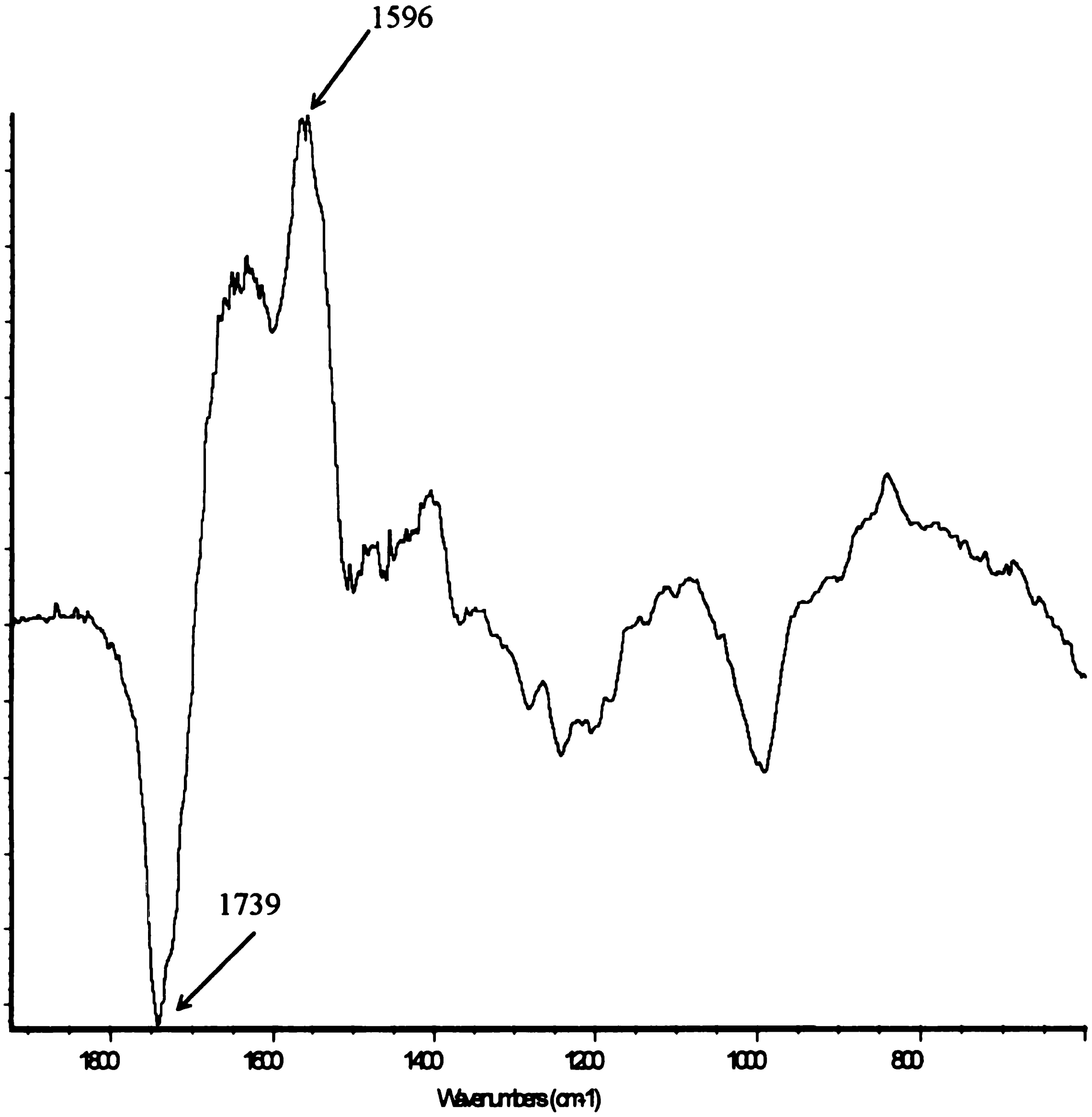

Figure 4.3 Subtraction of spectrum of untreated wood from that of Cu-MEA treated wood

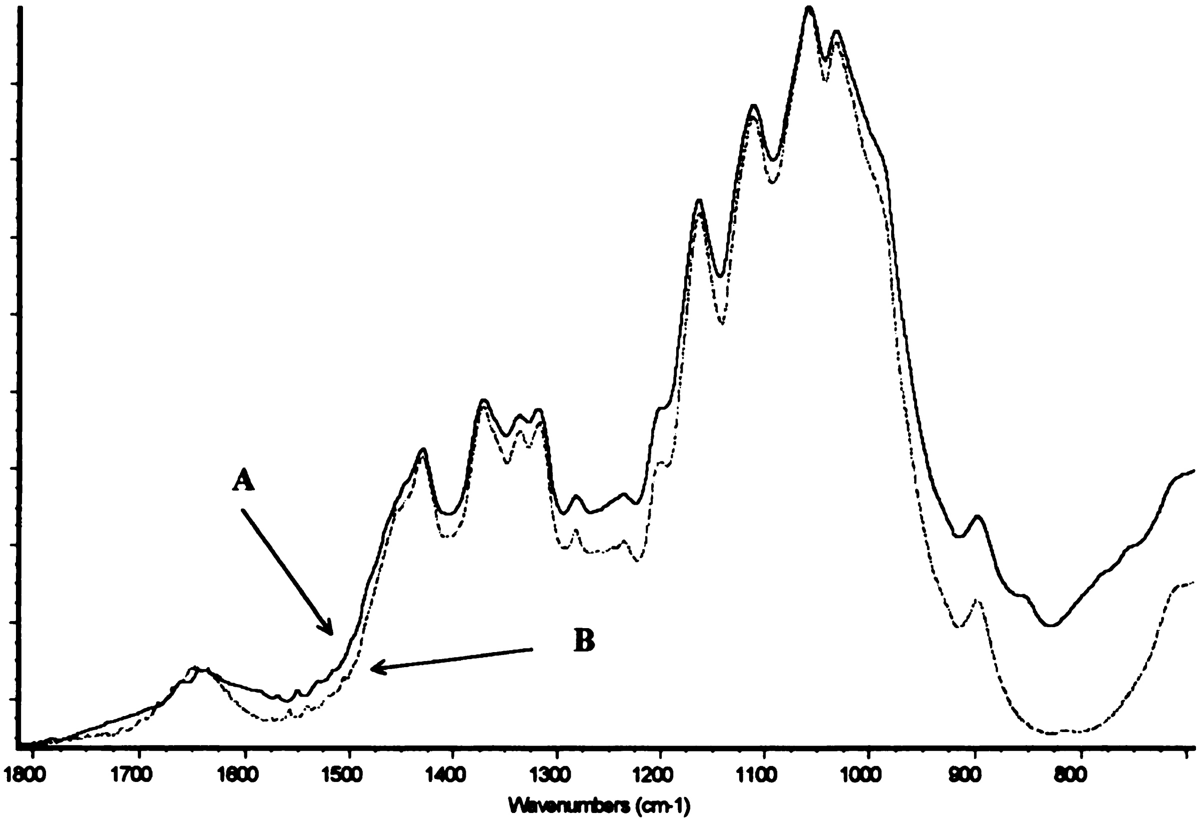

Figure 4.4 FTIR spectra of (A). Cellulose and (B). Cu-MEA treated cellulose

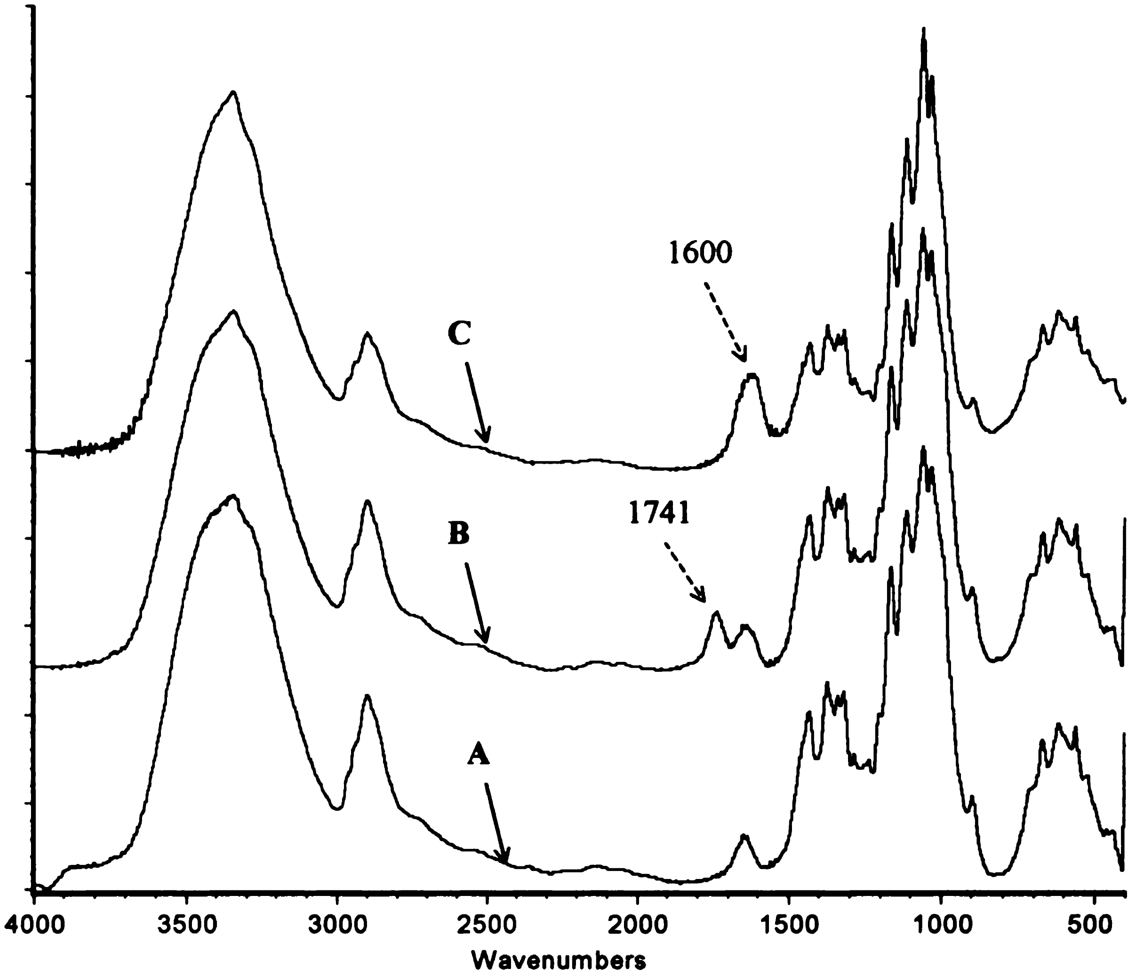

Figure 4.5 FTIR spectra of (A). Cellulose; (B). Oxidized cellulose and (C). Cu-MEA treated oxidized cellulose

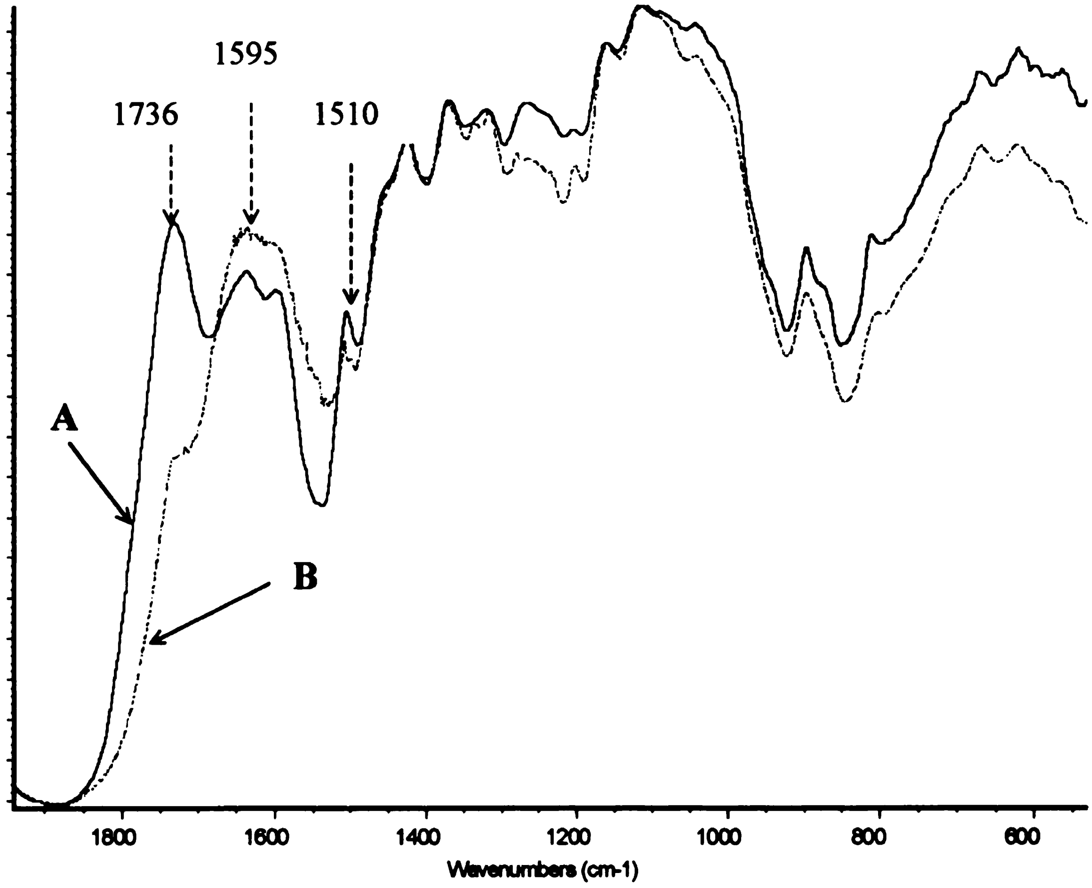

Figure 4.6 FTIR spectra of (A).Holocellulose and (B). Cu-MEA treated holocellulose

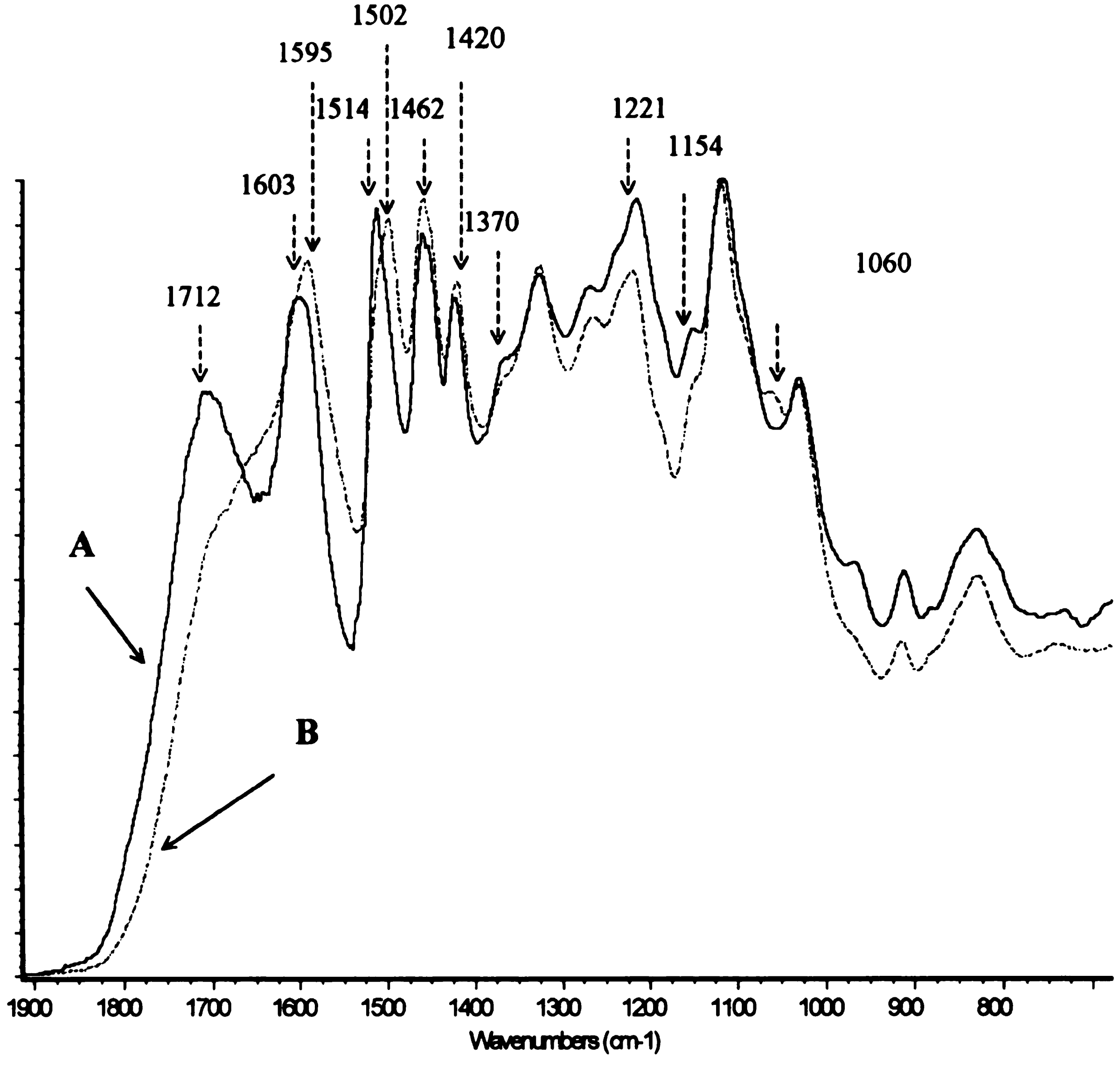

Figure 4.7 FTIR spectra of (A). Lignin and (B). Cu-MEA treated lignin

MEA treating solution. This small amount of copper may be due to the result of physical interactions, such as dipole-dipole, ion-dipole and Van der Waals interactions, of copper with cellulose. These results imply that cellulose plays only a minor role in copper absorption and aliphatic hydroxyl groups are inert in bonding copper in the treating conditions since cellulose contains a great amount of aliphatic hydroxyl groups. Figure 4.5 demonstrates the FTIR spectra of cellulose, oxidized cellulose and Cu-MEA treated oxidized cellulose. After oxidation of cellulose, a new band appeared at 1741 cm^{-1} due to the introduction of carboxylic acid. When the oxidized cellulose was treated with Cu-MEA solution, the band at 1741 cm^{-1} disappeared and the intensity of the band at 1600 cm^{-1} increased. The result confirmed that the carboxylic acid groups are the active sites for copper.

Figure 4.6 shows the spectra of holocellulose and Cu-MEA treated holocellulose. As was the case in Cu-MEA treated wood, the intensity of the band at 1736 cm^{-1}, assigned to carboxylic groups, minimized and was shown as a shoulder after Cu-MEA treatment. The intensity of the band at approximately 1595 cm^{-1} was also increased in treated holocellulose due to the shift of the carboxylic band. It has been reported that most carboxylic groups in wood are contributed by hemicellulose, for instance the uronic acid (Sjöström, 1989). These carboxylic groups can be attributed to copper absorption (0.6%) in a 1.0% Cu-MEA treated holocellulose because holocellulose consists of hemicellulose and cellulose and the copper absorbed by cellulose can be neglected. The weak band at 1510 cm^{-1} in holocellulose (Figure 4.6A) indicates the presence of small amount of lignin. After treatment, the band intensity was decreased. More detail on this band is discussed in the following paragraph.

The FTIR spectra of lignin and Cu-MEA treated lignin are demonstrated in Figure 4.7. The assignment of the band at 1712 cm^{-1} in lignin (Figure 4.7A) has always been difficult and controversial since unconjugated ketones, conjugated carboxylic acids and their esters absorb in the 1712 cm^{-1} region. It has been reported that saturated open chain ketones have a characteristic carbonyl stretching frequency of 1700-1715 cm^{-1} in the solid state. The lignin model compounds, guaiacyl acetone, ß-hydroxylconiferyl alcohol and 1-ethoxy-1-guaiacyl-2-propanone, showed absorption bands at 1705, 1709 and 1710 cm^{-1}, respectively (Hergert, 1971). This supports that the 1712 cm^{-1} band is due to carbonyl vibration in unconjugated ketones groups. However, Smith (1955) conducted comprehensive study on this band and pointed out that this band was caused by the esters of acids, such as p-hydroxybenzoic, vanillic, syringic, p-hydroxycinnamic and ferulic acids. This result was supported by Sarkanen *et al.* (1967b). Sarkanen *et al.* (1967b) also observed that treatment of ponderosa pine lignin with a buffer solution of pH 7 caused no change in the IR spectrum, suggesting that this band is not the absorption of carboxylic acid groups.

After treatment of lignin with Cu-MEA solution, the 1712 cm^{-1} absorption band diminished and the absorption at 1603 cm^{-1} shifted to 1595 cm^{-1} with a small intensity increase (Figure 4.7B). This case is very similar to that of Cu-MEA treated wood and holocellulose. It is easy to take it for granted that the 1712 cm^{-1} band is due to carboxylic acid. As mentioned above, this band is not caused by carboxylic acid. In addition, it has been reported that carboxylic acid content in lignin was very low (Sjöström, 1989). So, the disappearance of band at 1712 cm^{-1} is not due to the change in carboxylic acid. It should be noted that the pH of the Cu-MEA treating solution used in this study was about

10. With such an alkaline solution, the ester groups with absorption at 1712 cm^{-1} can be hydrolyzed into aromatic carboxylic acid groups (Sarkanen *et al.*, 1967b). When the carboxylic acid groups form, they can further interact with copper ion, leading to the formation of copper complex. This explains the decrease in band intensity at 1712 cm^{-1} and the increase in band intensity at 1595 cm^{-1}.

Normally the absorption band at around 1735 cm^{-1} (carboxylic acid) for hardwood, such as beech, is three times higher than the 1712 cm^{-1} absorption band (Faix, 1992). However, the 1712 cm^{-1} absorption band dominated over the 1735 cm^{-1} band in this case. The organosolv lignin used in this study was obtained from ALCELL process. Carboxylic acids would be expected to be esterified during ALCELL pulping in a mildly acidic ethanol/water mixture at approximate 200 °C (Goyal *et al.*, 1992). The expected reaction is shown below:

$$\text{Wood - COOH} + CH_3CH_2OH \xrightarrow{H^+} \text{Wood} - COOC_2H_5 + H_2O$$

It has also been reported that alkaline treatment of lignin could cause oxidative cleavage (Hergert, 1960). Treatment of the model compounds, such as guaiacyl acetone and the keto form of ß-hydroxylconiferyl alcohol, with mild alkali in the presence of air resulted in the loss of the 1712 cm^{-1} ketone carbonyl and its subsequent replacement upon acidification with a carboxylic acid group (Hergert, 1960). So if the absorption band at 1712 cm^{-1} in lignin (Figure 4.7A), is due to ketone carbonyl groups, it can also form carboxylic groups through oxidation under the treating conditions, and the carboxylic groups can further form carboxylate, causing an increase of band intensity at 1595 cm^{-1}.

The absorption bands at 1603, 1514, and 1420 cm^{-1} in lignin (Figure 4.7A) were assigned to aromatic skeletal vibration. The intensity and position of these bands are sensitive to the nature of ring substituents (Hergert, 1971). After treatment, the band at 1514 cm^{-1} shifted to 1502 cm^{-1} and the relative intensity of the 1514 cm^{-1} ring-stretching band and the band at 1462 cm^{-1} of C-H bonds was reversed. These changes can be explained that treatment could alter the aromatic ring substituents, for instance, the hydrolysis of aromatic esters and/or oxidative cleavage of ketone carbonyl groups.

The absorption bands at 1370 cm^{-1} and 1221 cm^{-1} in lignin (Figure 4.7A) have been assigned to phenolic O-H deformation by a considerable number of investigators (Kolboe and Ellefsen, 1962, Sarkanen *et al.*, 1967a and Hergert, 1971), although C-H deformation also absorbs in 1370 cm^{-1} and in 1220 cm^{-1} regions (Sarkanen *et al.*, 1967a). The intensities of these two bands decreased after treatment with Cu-MEA (Figure 4.7B), which is due to the ionization of phenolic hydroxyl groups into phenolic anion. The phenolic anion can further bond with copper to form copper phenolic complex. A new weak band, exhibited in treated lignin at 1060 cm^{-1} (Figure 4.7B), could be assigned to C-O stretching in copper phenolate complex. Another change in FTIR spectra after treatment is the 1154 cm^{-1} absorption band. This band is normally assigned to C-O stretching from ester groups (Colthup *et al.*, 1964). The lowered intensity of this band in Cu-MEA treated lignin is an indication of alkaline hydrolysis of ester groups.

Three main ionizable groups, namely carboxylic acid groups, phenolic hydroxyl groups and alcoholic hydroxyl groups, are present in wood. Of these, the majority of carboxylic groups are carried by hemicellulose, and lignin contains only a comparatively few carboxylic groups (Sjöström, 1989). Lignin mainly contributes phenolic hydroxyl groups and ester groups, and the ester groups can be hydrolyzed to carboxylic groups under both acidic and alkaline conditions. Cellulose can only contribute alcoholic hydroxyl groups. When wood is treated with copper amine preservative, these groups are the possible bonding sites for copper ions. According to Serjeant and Dempsey (1979), carboxylic acid groups are ionized in neutral or even weakly acidic conditions, a rather high pH above 10 is needed for ionization of phenolic hydroxyl groups, and a very strong alkali is needed for ionization of alcoholic hydroxyl groups. When wood is treated with copper amine solution, carboxylic groups and phenolic groups can be easily ionized during treatment. They are responsible for the bonding of copper. In addition, aromatic esters in lignin can be hydrolyzed into aromatic carboxylic groups, which act as extra bonding sites for copper. These hypotheses have been confirmed by the FTIR spectra. The dissociation of alcoholic hydroxyl groups was minimal in the treating solution used in this study. This accounts for the negligible absorption of copper in cellulose and no change in FTIR spectrum of cellulose after being treated with copper amine.

4.5 Conclusions

Diffuse reflectance FTIR (DRIFT) spectra of cellulose, hemicellulose and lignin were analyzed. The carboxylic acid groups in hemicellulose and the phenolic groups in lignin are the major bonding sites for copper. In addition, aromatic esters groups and/or ketone groups, which can be changed to carboxylic acid groups through alkaline hydrolysis or oxidative cleavage, are other potential bonding sites for copper.

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Chapter 5

Electron Paramagnetic Resonance Spectroscopic (EPR) Analysis of Copper Amine Treated Wood

5.1 Abstract

The structures of copper complexes in copper amine treated wood samples were elucidated by the application of electron paramagnetic resonance spectroscopy. Axial spectra were observed for all treated samples irrespective of the formulations. The $A_{||}$ and $g_{||}$ of all the axial spectra indicated that the stereo-structure of copper complexes in copper amine treated wood is tetragonal-based octahedral or square-based pyramidal. Comparison of electronic parameters of $A_{||}$ and $g_{||}$ in treated wood with those in treating solution and those reported in literature suggests that the interactions of wood with copper amine is through complexation in which functional groups from wood complex with copper amine perpendicularly. The copper complexes in both treating solution and treated wood are in the form of CuN2O2.

5.2 Introduction

Copper amine is one of the main ingredients of ammoniacal copper quat-type D (ACQ-D), copper dimethyldithiocarbamate (CDDC), and copper azole (AWPA, 1998). Chemically speaking, this system is a series of cupric complexes in which different type of ethanolamines act as bidentate chelating agents through amino and hydroxyl groups. At high pH solution system, deprotonation of the hydroxyl groups and formation of stable chelate rings are proposed (Tauler and Casassas, 1986). The chemical interactions between this copper amine chelating ring complex and wood are not well understood.

While a considerable number of methods have been employed to investigate the interaction between copper-based wood preservatives and wood, only a few are suitable to study the chemical and electronic structure of copper in treated wood. To date, FTIR (Ostmeyer *et al.*, 1989) and XPS (Kamdem *et al.*, 1998) have been used to obtain valuable information on bonding and valency state of the copper in treated wood. However, these techniques cannot elucidate the stereochemistry of copper complexes formed in copper-based preservative treated wood, such as the ligand field information and the configuration of mono or divalent copper complexes. Previous work has shown that electron paramagnetic resonance (EPR) can be successfully used to study the copper bonding environment and the stereochemical structure of copper complexes in copper-based preservative treated wood substrate (Plaket, 1987; Pohleven *et al.*, 1994; Hughes *et al.*, 1994).

The EPR spectra of transition metal ion complexes contain a wealth of information about their electronic structures. Plaket *et al.* (1987) have performed EPR spectroscopic analysis of radiata pine treated with CCA and copper sulfate and they found no evidence of copper complexation with lignin and concluded that copper (II) in copper sulfate treated wood was in the form of hydrated copper (II) ion ($Cu(H_2O)_6^{2+}$) bound to wood through hydrogen bonding. Hughes *et al.* (1994) observed the presence of a number of different copper complexes in preservative treated *Pinus sylvestris* as a function of the formulation of copper preservatives. Their study also showed the existence of immobile copper ions in all treated samples. The EPR spectra of the ammoniacal copper treated wood indicated that the $A_{||}$ and the $g_{||}$ tensors of copper were different from those in the original ammoniacal copper solution, suggesting that the ammonia ligands of copper in the original treating solution have been replaced by oxygen (Ruddick, 1992).

EPR was used in the current study to investigate the interactions of copper amine with wood and to describe the possible stereochemistry copper complex in treated wood. Such a study is of great importance in understanding the retention, penetration and fixation of copper amine treated wood and in predicting the biological performance and the stability of such a system.

5.3 Theoretical Principles of the EPR of Copper Complexes (Drago, 1992)

On application of a magnetic field, different energy states arise from the interaction of an unpaired electron spin moment (given by $m_s = \pm½$ for a free electron) with the magnetic field, the so-called electron Zeeman effect. The "Zeeman Hamiltonian" that describes the interaction of an electron with a magnetic field is:

$$\hat{H} = g\beta B S_z$$

where g is Landé splitting factor (2.0023193 for a free electron)

β is the electron Bohr magneton, $e\hbar/2m_ec$, which has the value of 7.274×10^{-24} Joule/Tesla

B is the applied field strength

S_z is the spin operator

when this Hamiltonian operates on α spin and β spin corresponding to $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$, the splitting occurs (Zeeman splitting). The energy difference ΔE for a single electron ($m_s = \pm\frac{1}{2}$), found from the Hamiltonian, is given by:

$$\Delta E = g\beta B$$

The direction of the field has been taken as the axis of quantisation (z).

Divalent copper ion Cu^{2+} with a $3d^9$ electronic configuration has one unpaired electron in d-orbital. It has an effective spin of $s = \frac{1}{2}$ and associated spin angular momentum of $m_s = \pm\frac{1}{2}$ resulting in a doubly degenerate spin energy state in the absence of a magnetic field. The spin energy degeneracy is removed after an application of a magnetic field. Besides the interaction of electron spin moment with the magnetic field, there is also an interaction between magnetic field B and the magnetic moment due to the orbital angular momentum of the electrons. The total interaction, assuming Russell-Saunders coupling, is given by:

$$\hat{H} = \beta B(L + gS_z)$$

where L is the orbital angular momentum of the electrons.

The Zeeman splitting of the ground state can be observed in an electron spin resonance experiment. The orbital angular momentum is "quenched" for the ground states of most copper (II) complexes, but spin-orbit coupling mixes-in some contributions from excited states, the extent being expressed by the multiplet splitting factor "g" in the energy equation.

$$hv = g\beta B$$

Where h is Planck's constant and ν is frequency.

In practice, three types of EPR spectra of divalent copper are observed, namely, isotropic spectra, axial spectra and rhombic spectra. Of these, axial is the most common situation for copper complexes, where copper is in a tetragonally distorted environment. Previous study has also shown that copper complexes in wood are in axial configuration (Packett *et al.*, 1987). The axial spectra of copper complexes exhibit a strong absorption to higher field at $g_\perp$ and weak absorption to lower field at $g_{||}$. The hyperfine splitting, $A_\perp$, due to the nuclear magnetic moment of the Cu^{2+} at $g_\perp$ is too small to differentiate. The hyperfine splitting $A_{||}$, arising from the nuclear magnetic moment of the Cu^{2+} at $g_{||}$, is usually much greater, having typical values from 150 to 250×10^{-4} cm^{-1}, and four features at $g_{||}$ are often resolved.

5.4 Materials and Methods

5.4.1 Materials

Kiln-dried southern pine (SP) sapwood was used for the current study. SP was ground into sawdust to pass 60 mesh. Organosolv lignin was purchased form Aldrich Chemical Co. Oxidized cellulose was prepared by oxidation of cellulose as described in Chapter 4. Copper amine treating solutions were made by mixing copper compounds with ethanolamine, such as monoethanolamine (MEA), 2-methylamino-ethanol (DMEA) and N, N-dimethyl-ethanolamine (DMeEA) (Table 5.1). The molar ratio of amine to copper was kept constant at 4.

Table 5.1 Copper amine formulations used for wood substrate treatment *

Wood substrates	Copper amine formulations	pH
Wood	Cu-MEA	10.8
	Cu-MEA	10.1
	Cu-MEA	9.3
	Cu-MEA	9.1
	Cu-MeEA	10.8
	Cu-DMeEA	10.6
	$CuSO_4$ solution	4.1
	$Cu(NO_3)_2$ solution	4.0
Lignin	Cu-MEA	10.8
Oxidized cellulose	Cu-MEA	10.8

* The copper concentration in all the formulations is 1.0% by weight

5.4.2 Treatment

About 2.5 grams of wood substrates were mixed with 50 grams of copper amine (Cu-EA) solution containing1.0 % elemental copper in 100ml flasks. The flasks were sealed and agitated on a wrist-shaker for 24 hours. After the agitation, samples were filtered through glass fiber filters and washed continuously with deionized water until the conductivity of the eluent water was constant. The purpose of continuous washing with water was to minimize physical absorption of copper in treated samples. The treated and water-washed samples were air-dried for two weeks and analyzed by EPR.

5.4.3 Electron Paramagnetic Resonance Spectroscopy (EPR)

EPR spectra were recorded on a Bruker ESP 300E X-band spectrometer at 9.5 GHz. The temperature was controlled either with flowing liquid helium or with a temperature controller. The operating conditions were: 100 kHz field modulation, 4.014 G modulation amplitude and 10.24 ms time constant. For liquid copper amine solution, the sample was put into the holder and cooled by liquid helium, and EPR spectrum was acquired at 6 Kelvin. For solid samples, EPR spectra were obtained at room temperature.

5.5 Results

EPR axial spectra of all wood samples treated with the formulation used in this study are illustrated in Figure 5.1 to 5.11. They all present a higher $g_{\perp}$ absorption and a relative weaker $g_{||}$ absorption. The hyperfine splitting of $A_{||}$ are well resolved and the $A_{\perp}$ is too small to be resolved. The G values, which is equal to $(g_{||}-2)/(g_{\perp}-2)$, are greater than 4. It has been reported that a G greater than 4 is specific to an axial type of EPR spectra and less than 4 specific to a rhombic type of EPR spectra (Hathaway and Billing, 1970).

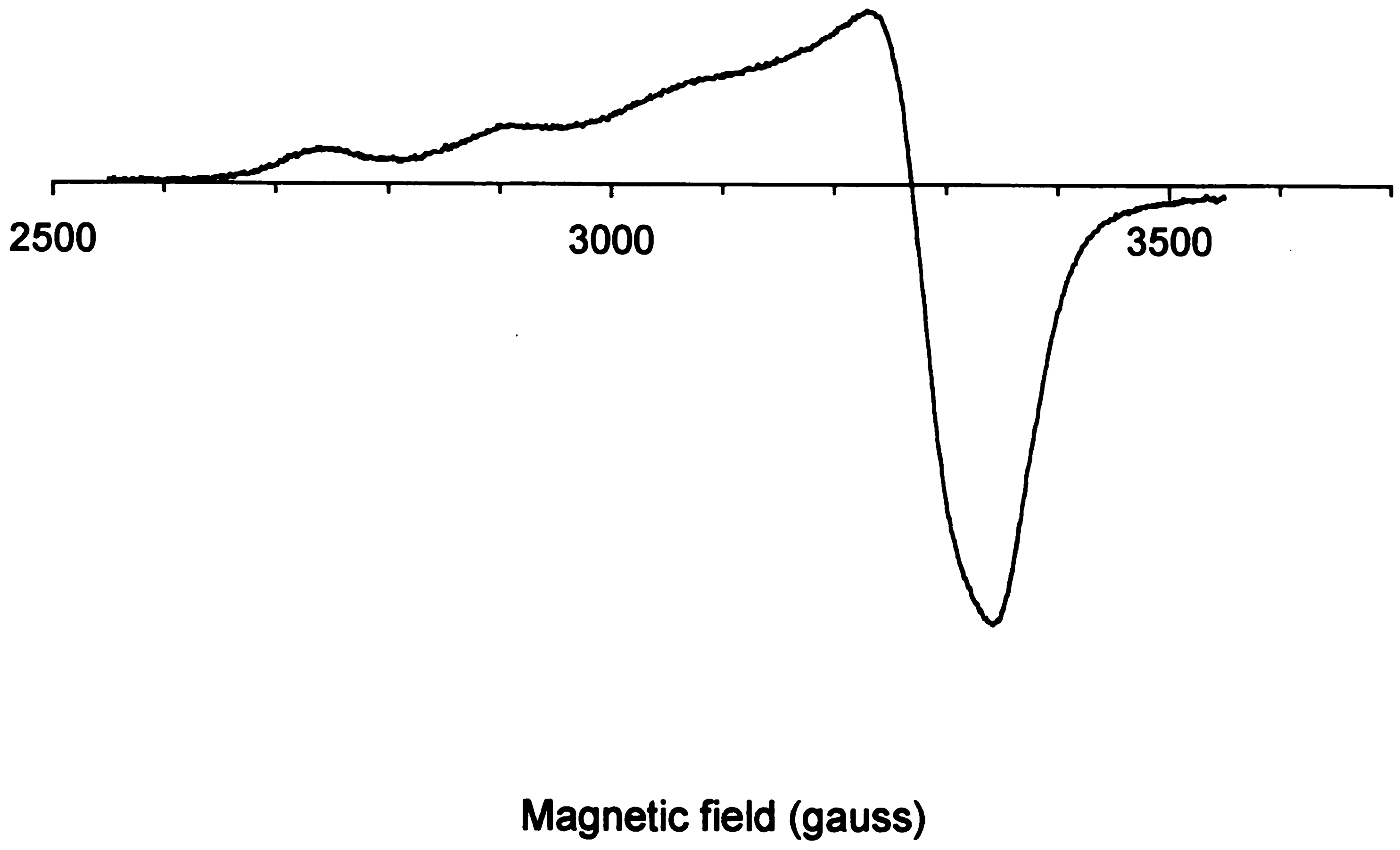


Figure 5.1 EPR spectrum of Cu-MEA frozen solution

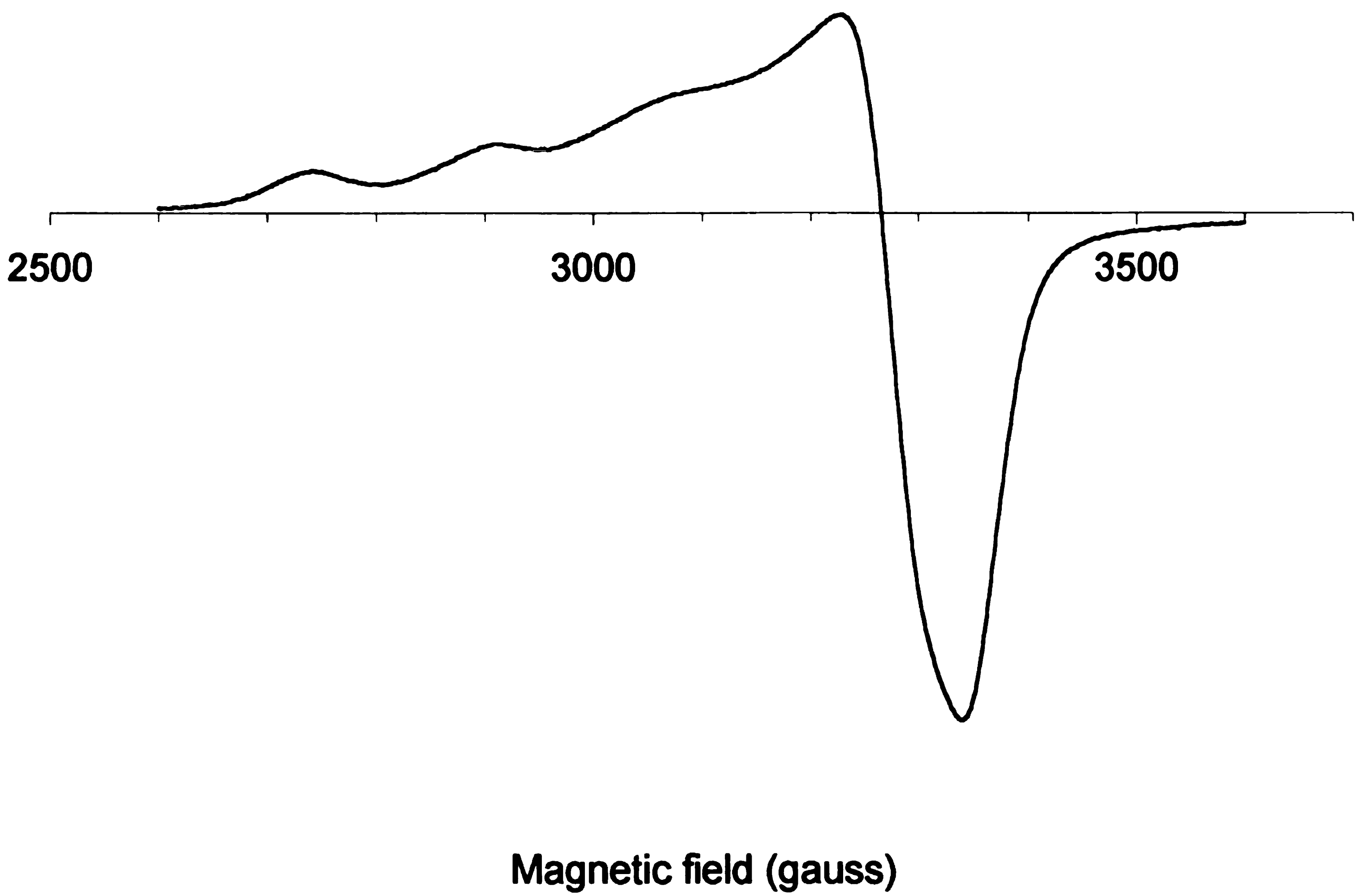


Figure 5.2 EPR spectrum of wood treated with Cu-MEA at pH of 10.8

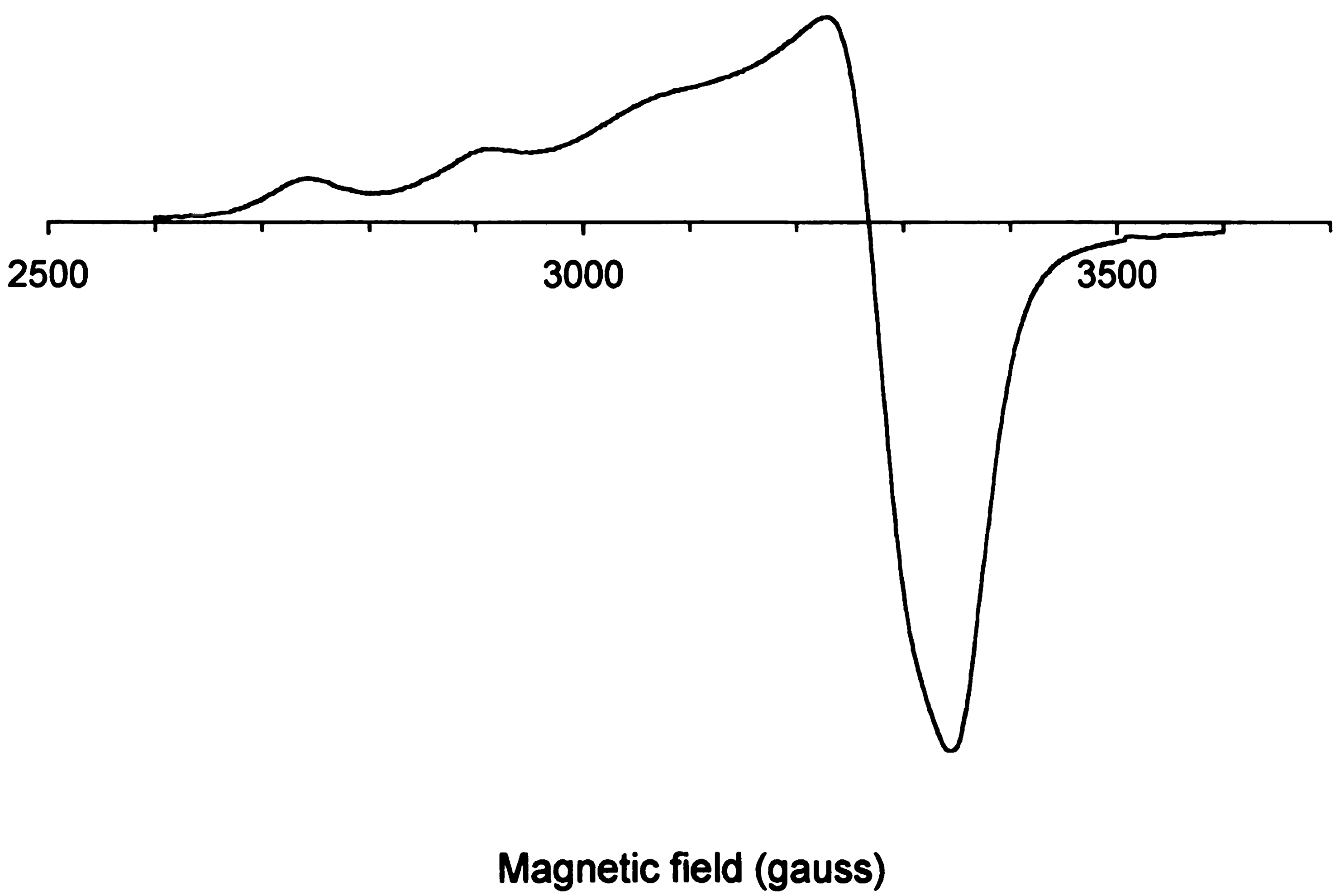


Figure 5.3 EPR spectrum of wood treated with Cu-MEA at pH of 10.1

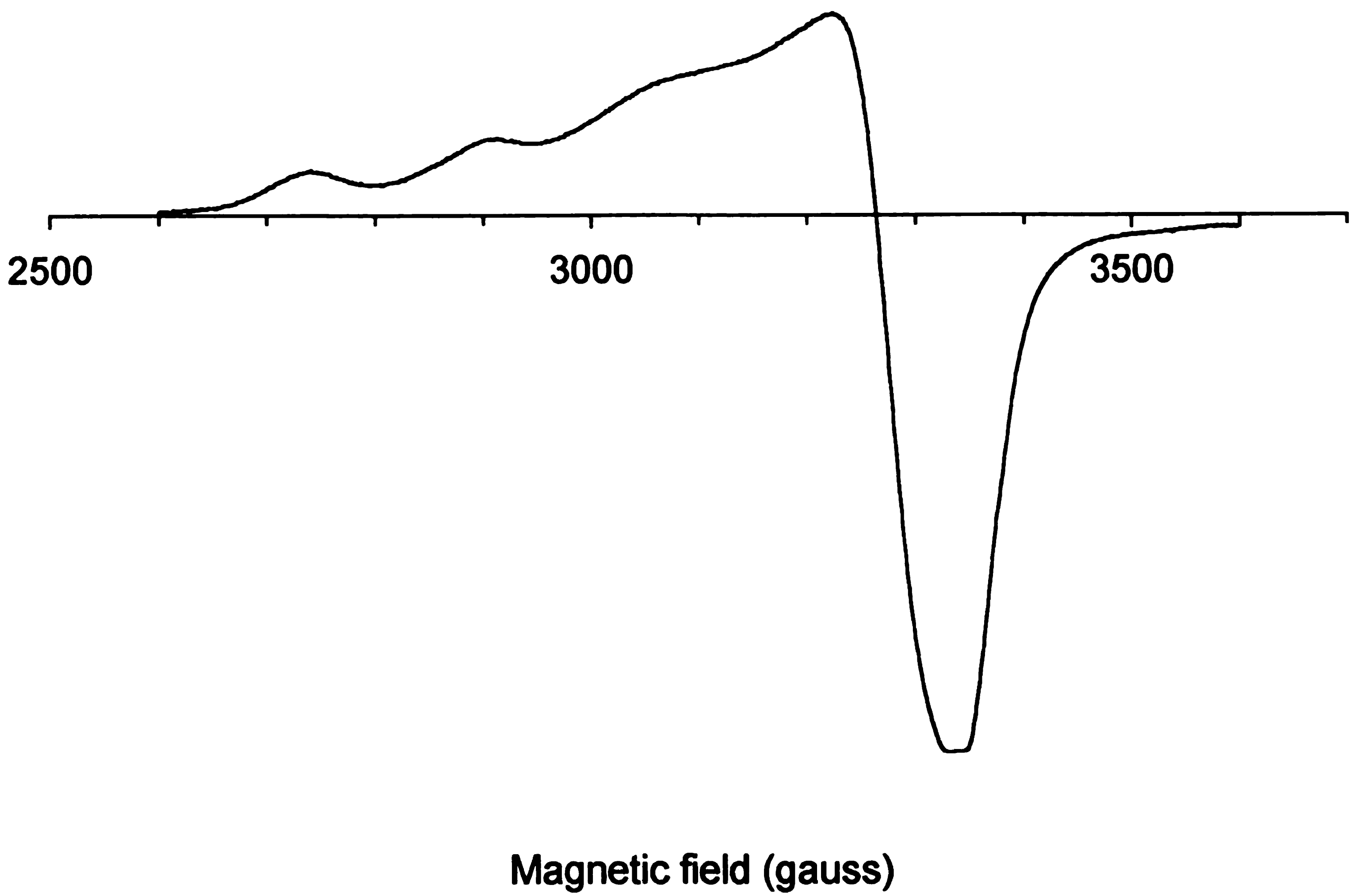


Figure 5.4 EPR spectrum of wood treated with Cu-MEA at pH of 9.3

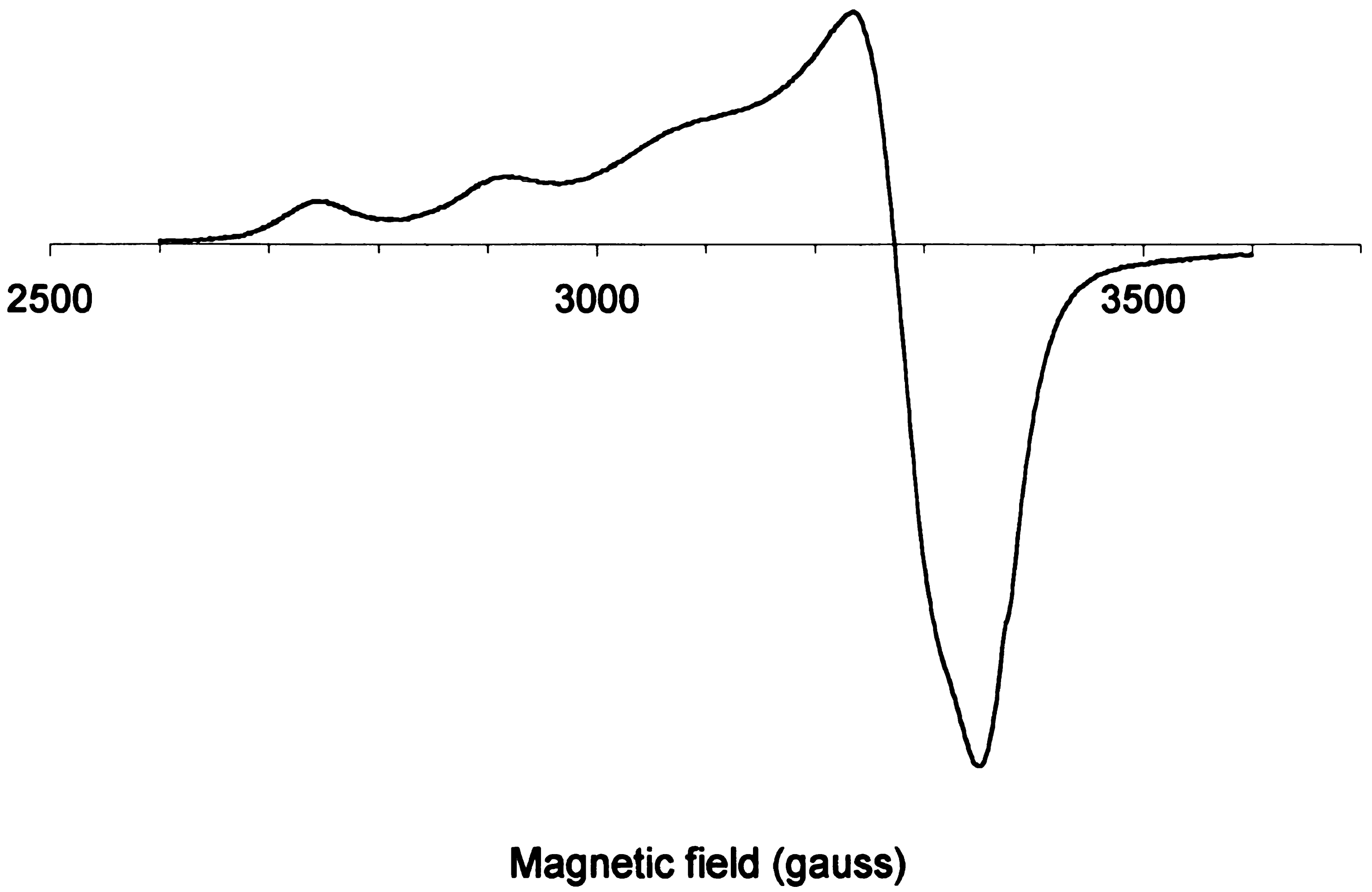


Figure 5.5 EPR spectrum of wood treated with Cu-MEA at pH of 9.1

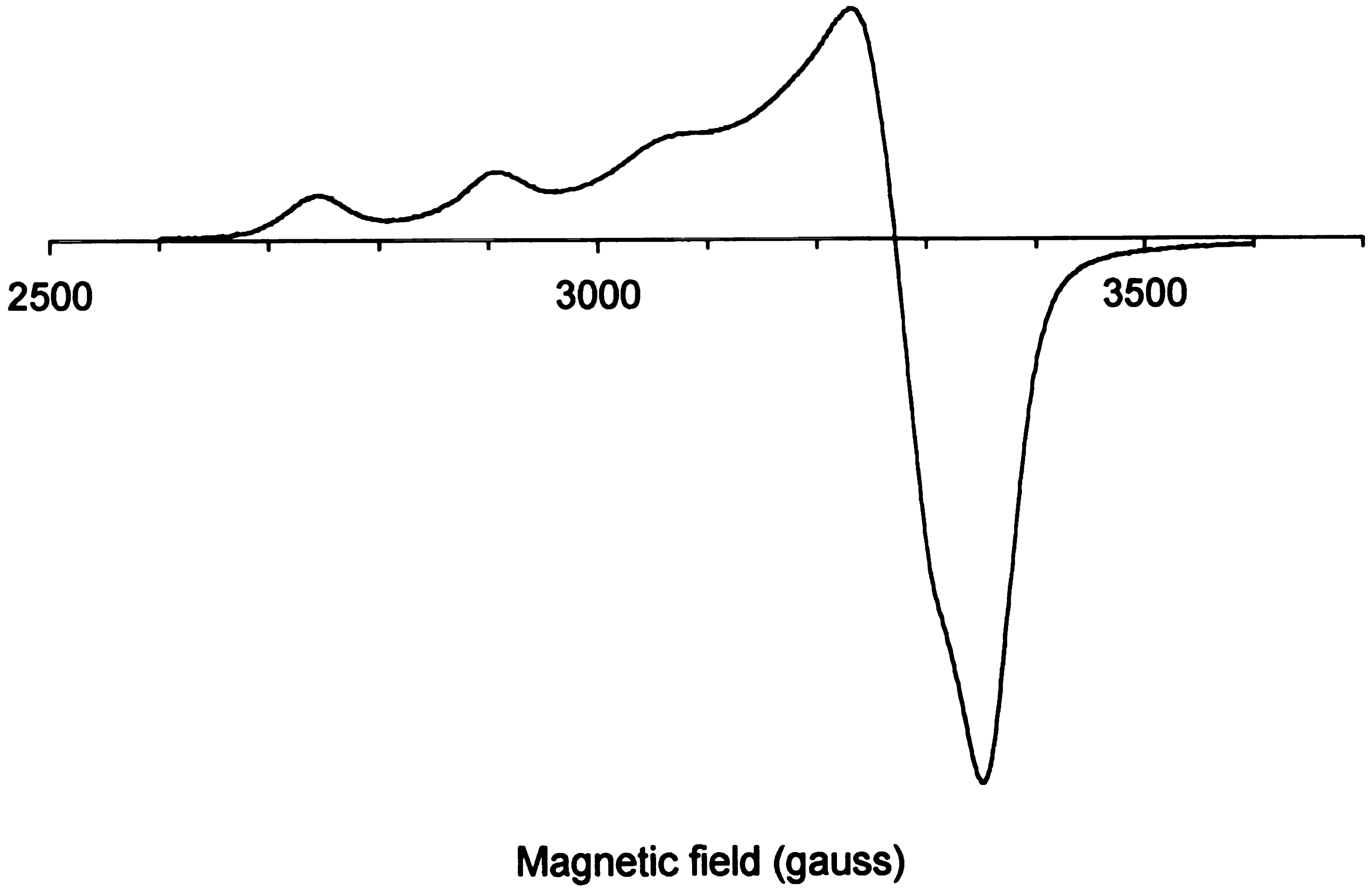


Figure 5.6 EPR spectrum of wood treated with Cu-MeEA

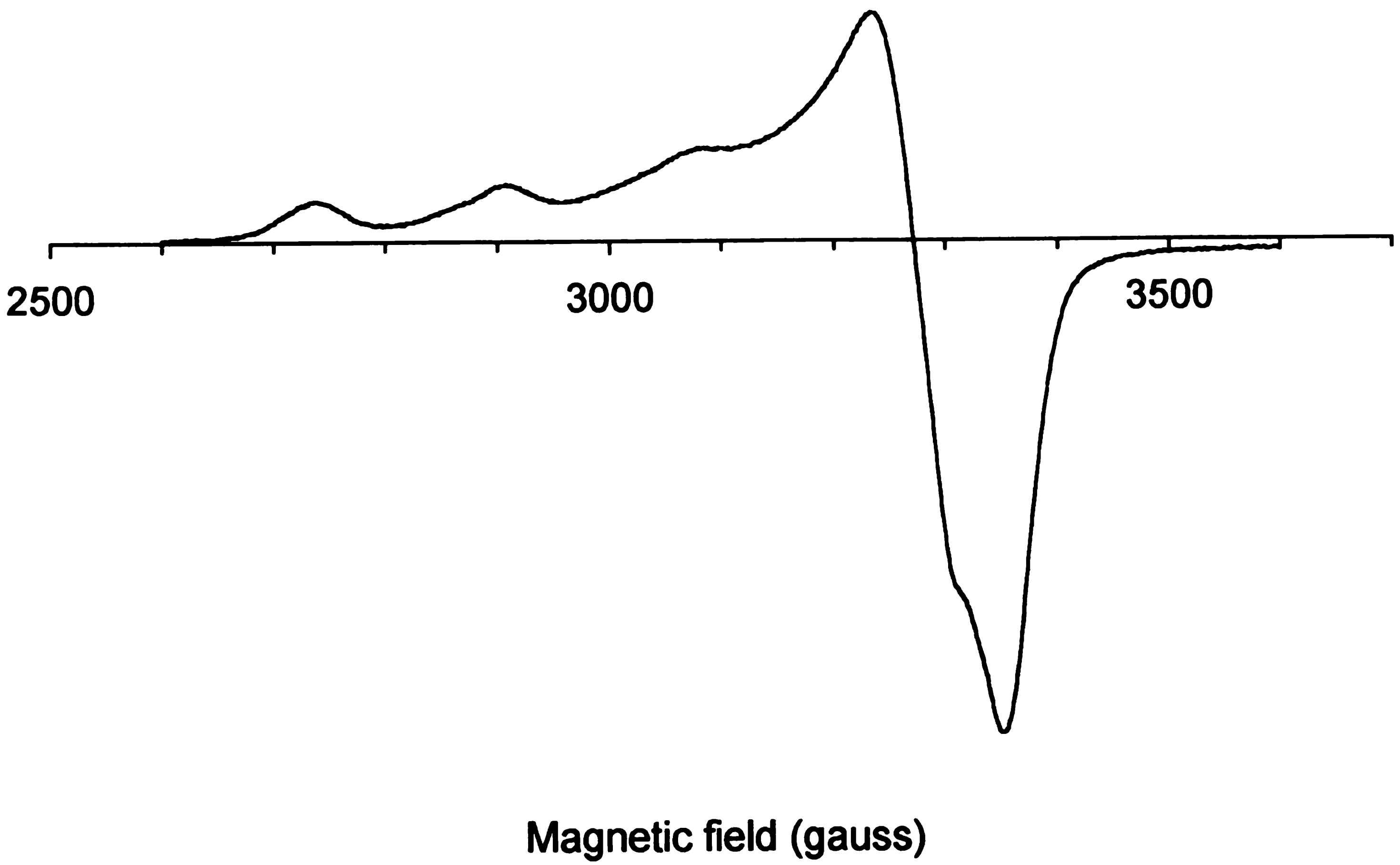


Figure 5.7 EPR spectrum of wood treated with Cu-DMeEA

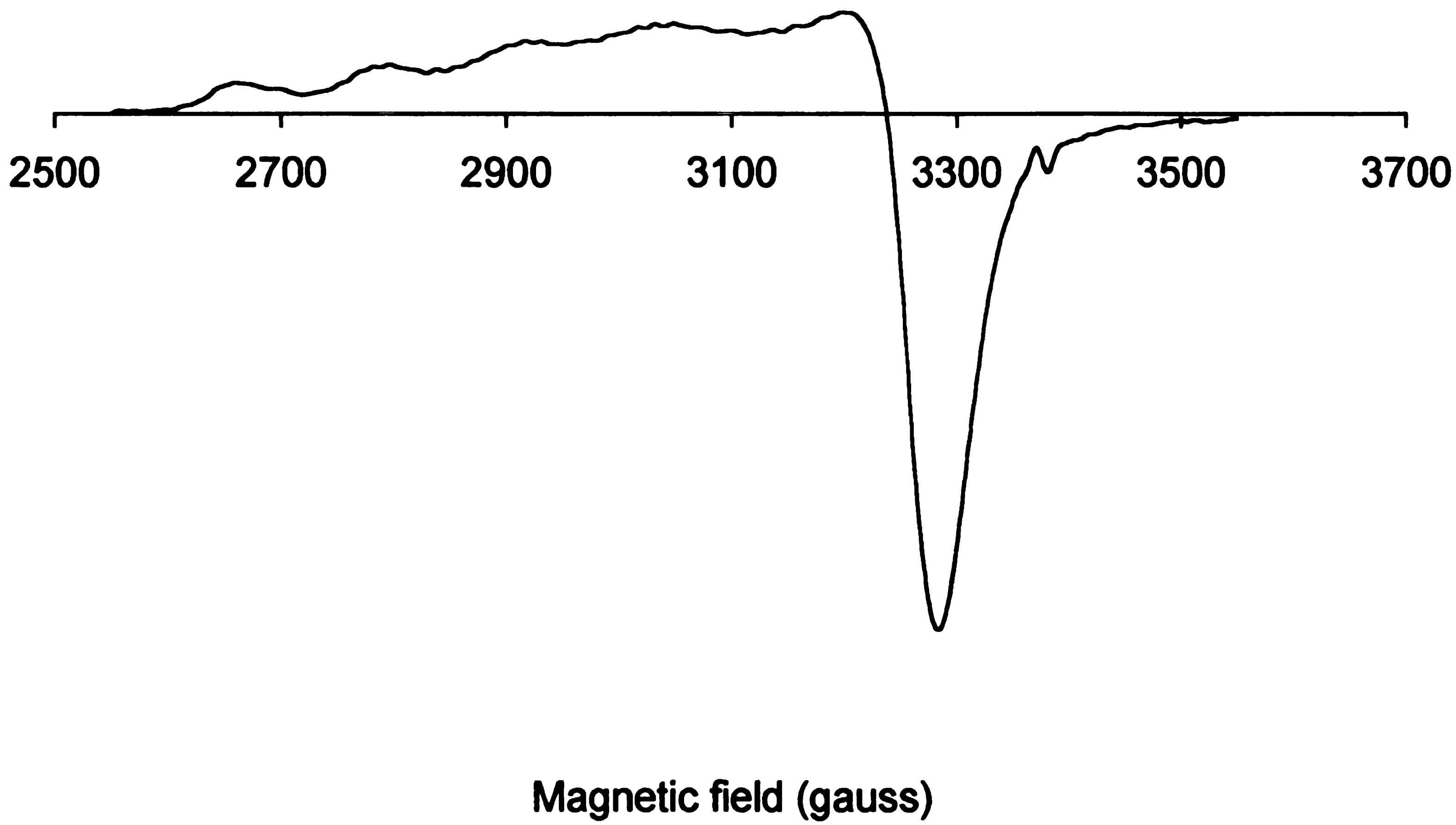


Figure 5.8 EPR spectrum of wood treated with CuSO4 solution

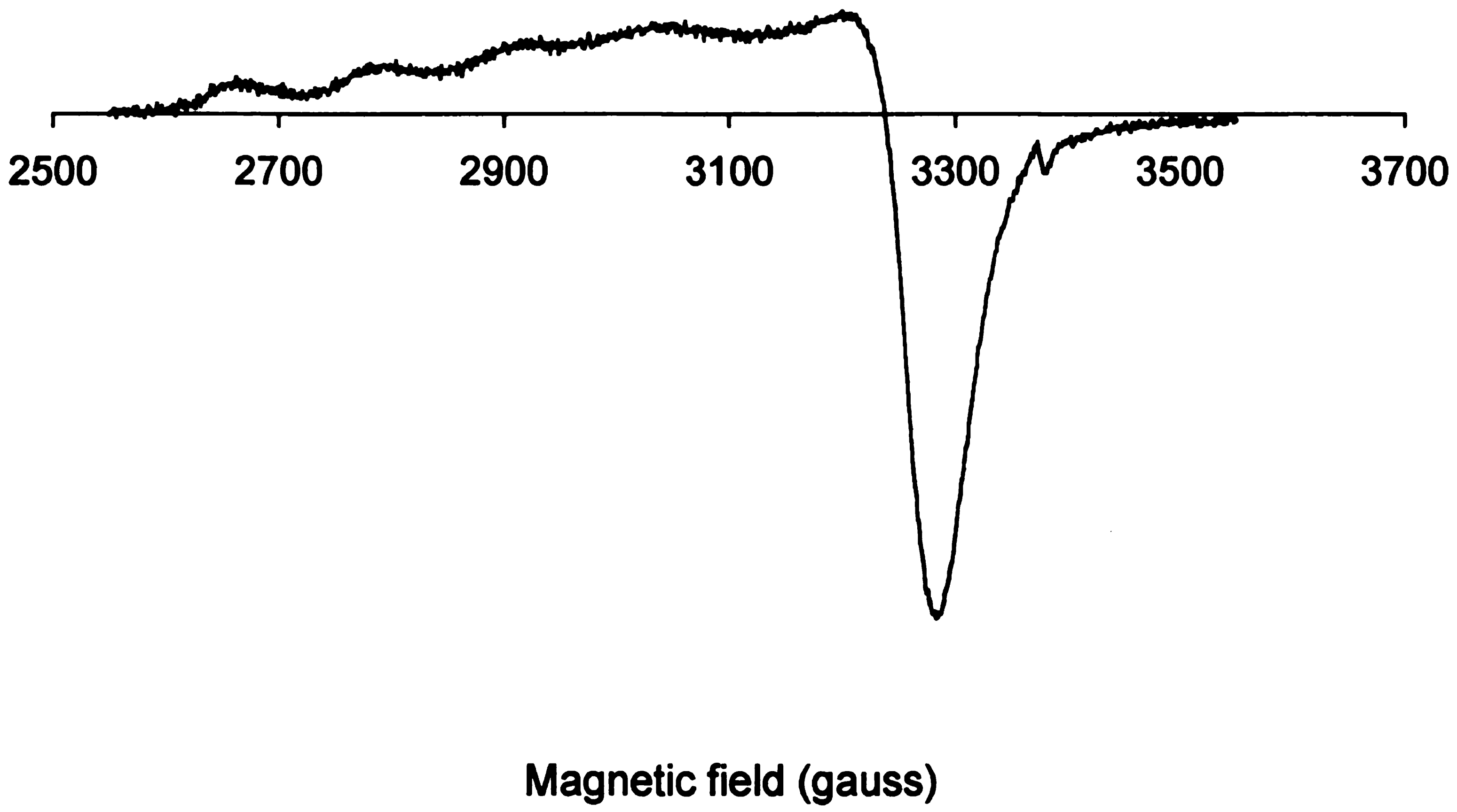


Figure 5.9 EPR spectrum of wood treated with Cu(NO3)2 solution

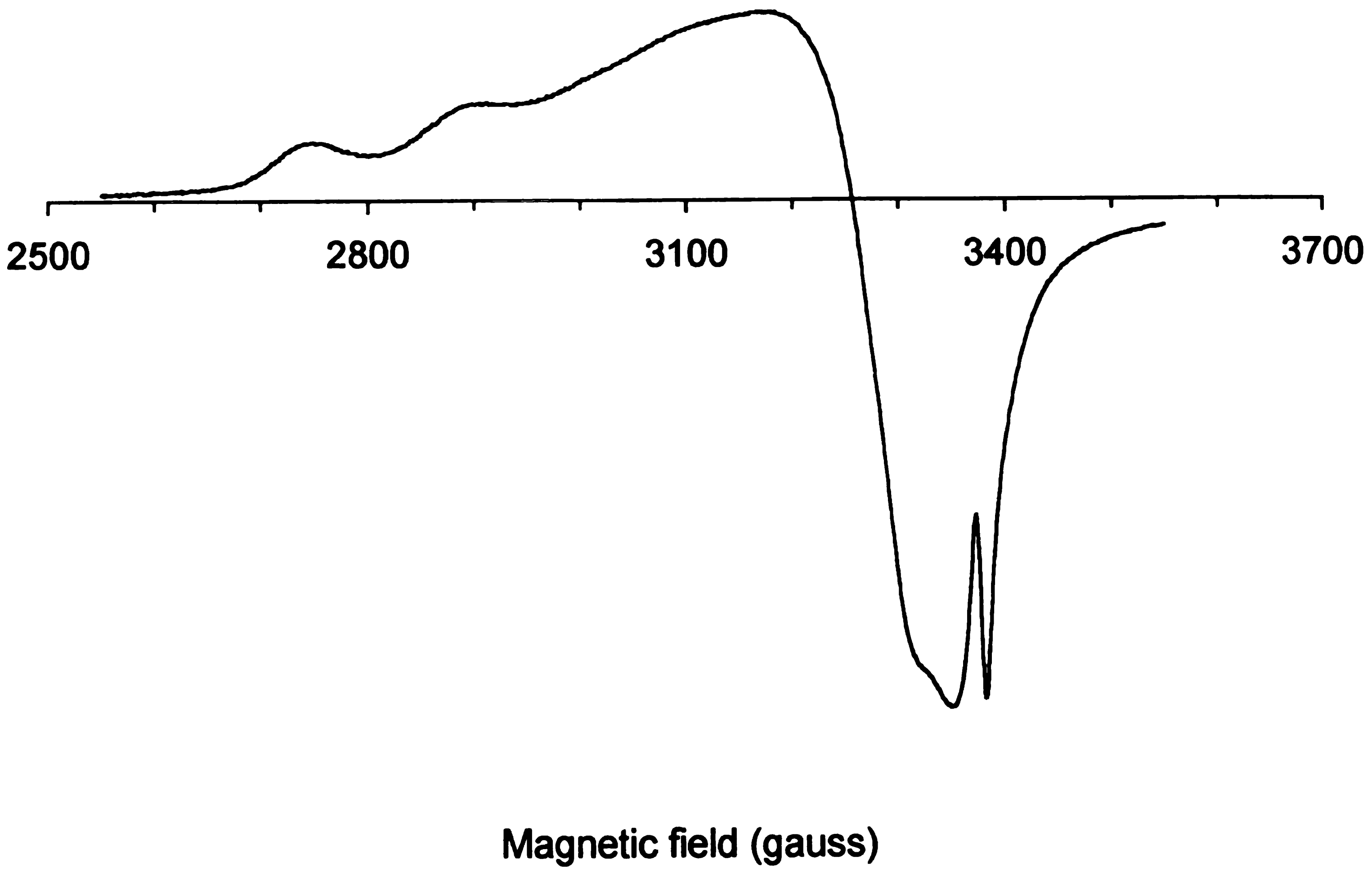


Figure 5.10 EPR spectrum of lignin treated with Cu-MEA

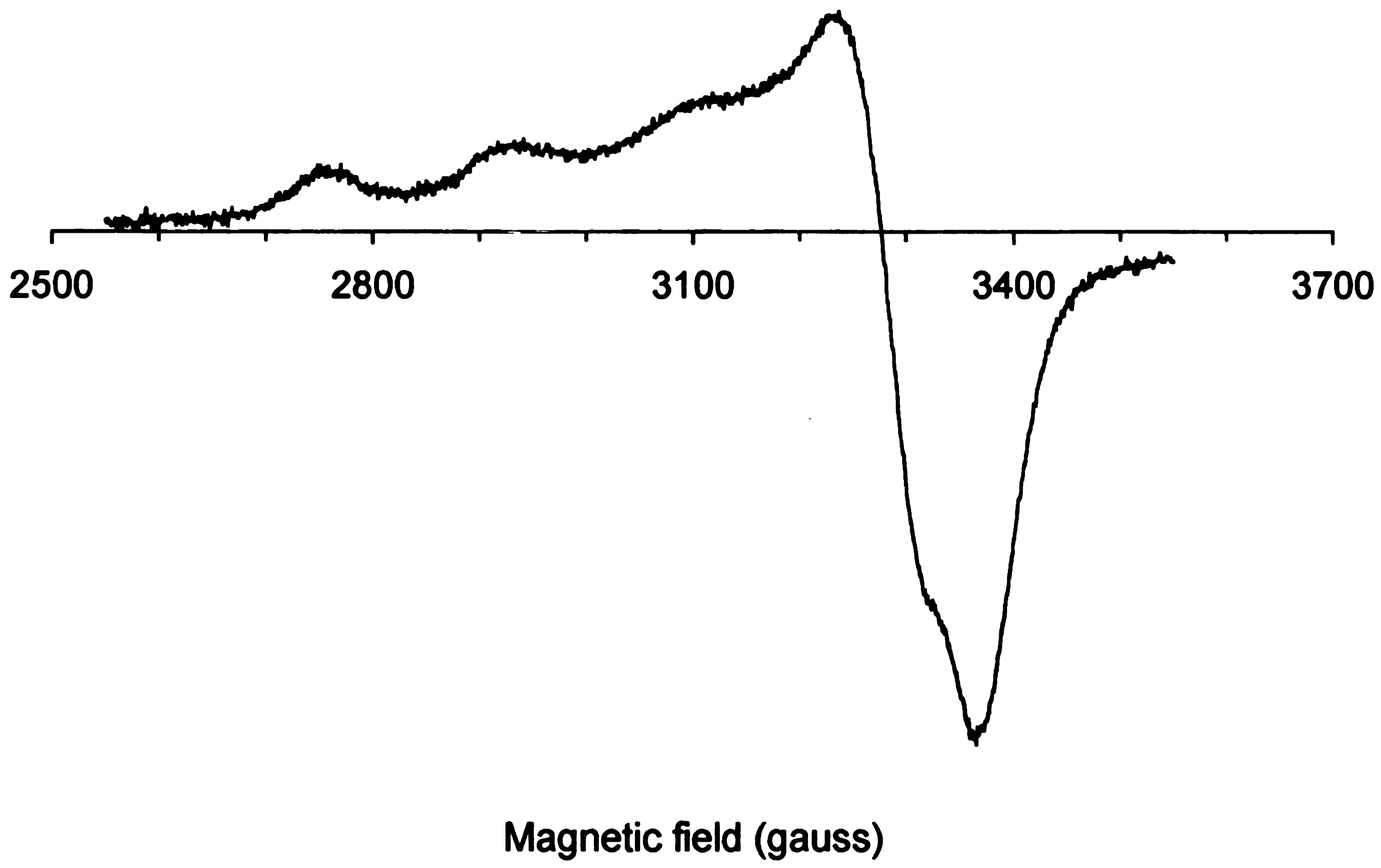


Figure 5.11 EPR spectrum of oxidized cellulose treated with Cu-MEA

The Hamiltonian parameters are listed in Table 5.2. The $g_{||}$ parameters for copper amine solution and copper amine treated samples are in the range of 2.2 to 2.3.

EPR spectrum of copper monoethanolamine frozen solution is illustrated in Figure 5.1. The A and g values are given in Table 5.2. The value of $A_{||}$ (17.1mK) is smaller and the value of $g_{||}$ (2.263) is greater than those parameters in copper ammoniacal solution where copper metal center is ligated with four nitrogen (CuN4) (Xie *et al.*, 1995). In copper amine solution, copper is ligated with 2 nitrogen and 2 oxygen (CuN2O2) (Casassas *et al.*, 1989). The replacement of N by O will reduce the value of $A_{||}$ and increase the value of $g_{||}$ because nitrogen (N) is more electron dense than oxygen (O).

Figure 2 shows the EPR spectrum of copper amine treated wood with $g_{||}$ of 2.271 and $A_{||}$ of 16.9 mK. The $g_{||}$ and $A_{||}$ parameters are close to those of copper amine complex in solution. Increase in the pH of the treating solution from 9.1 to 10.8 had a slight effect on the $g_{||}$ and $A_{||}$ of copper in treated wood (Table 5.2). Figure 5.3-5.5 show the EPR spectra of wood treated with copper amine at different pH conditions.

When the ligand was changed from MEA to DMEA and DeMEA, EPR spectra exhibited a shoulder on $g_{\perp}$ absorption (Figure 5.6 and 5.7). Hughes *et al.* (1994) observed the same phenomenon in their EPR study of copper complexes. They also noted a further $A_{||}$ splitting in the $g_{||}$ region, and they attributed this to the presence of two forms of copper in the treated timber. In the current study, no splitting on $A_{||}$ in the $g_{||}$ region were observed. The shoulder absorption in the $g_{\perp}$ region is likely due to the fourth feature of hyperfine splitting from $A_{||}$ since only 3 $A_{||}$ features are observed in the $g_{||}$ region. Compared to Cu-MEA treated wood, Cu-DMEA and Cu-DeMEA treated wood have a slight decrease in $g_{||}$ and a slight increase $A_{||}$. This may be attributed to the addition of

Table 5.2 EPR parameters of Southern pine treated with copper amine solutions

Samples	$g_{\parallel}$	$g_{\perp}$	G[a]	$A_{\parallel}$, mK[b]
Cu-MEA frozen solution	2.263	2.062	4.24	17.1
Wood treated with				
Cu-MEA, pH = 10.8	2.271	2.059	4.59	16.9
Cu-MEA, pH = 10.1	2.267	2.061	4.38	17.3
Cu-MEA, pH = 9.3	2.265	2.063	4.21	17.6
Cu-MEA, pH = 9.1	2.264	2.065	4.06	17.5
Cu-MeEA, pH = 10.8	2.263	2.06	4.38	17.8
Cu-DMeEA, pH = 10.6	2.258	2.059	4.37	17.9
CuSO4 solution, pH = 4.1	2.413	2.074	5.58	14.1
Cu(NO3)2 solution, pH = 4.0	2.382	2.068	5.62	14.5
Lignin treated with				
Cu-MEA, pH = 10.8	2.287	2.055	5.22	15.9
Oxidized cellulose treated with				
Cu-MEA, pH = 10.8	2.259	2.053	4.89	17.4

a: $G = (g_{\parallel} - 2) / (g_{\perp} - 2)$

b: mK is milikaisers (thousandths of a wavenumber cm^{-1})

electron-donating methyl groups. The presence of methyl groups in DMEA and DeMEA introduces steric effect that influences the stability of copper amine complex (Hancock and Nakani, 1984). It was suggested that the EPR parameters of copper were determined by the chemical nature and charge state of the close-lying ligand atoms to copper atom, and were not directly correlated with thermodynamic parameters which govern stability of metal-ligand complexes (Peisach and Blumberg, 1974).

To elucidate the effect of amine ligands on EPR parameters, copper sulfate and copper nitrate treated wood was studied. Although copper sulfate and copper nitrate treated wood exhibited axial spectra as illustrated in Figure 5.8 and 5.9, the value of $A_{||}$ is much smaller and $g_{||}$ is greater than those obtained with copper amine treated wood (Table 5.2 and Figure 5.13). This may be explained by the presence of only oxygen-copper bondings in copper sulfate and copper nitrate treated wood. With the small hyperfine splitting, four features of $A_{||}$ are observed in the $g_{||}$ region (Figure 5.8 and 5.9).

Figure 5.10 shows the EPR spectrum of copper amine treated lignin, which has a relatively smaller $A_{||}$ and larger $g_{||}$. In addition, a strong free radical signal was also observed in the spectrum. The formation of free radicals was tentatively attributed to the abstraction of electrons from phenolate anions by Cu(II) to form phenoxy radicals and Cu(I) (Landucci, 1978). The Cu(I) was subsequently oxidized to Cu(II) by oxygen in the air.

No EPR signal was obtained on copper amine treated cellulose. This is due to the lower absorption of copper by cellulose. Only 0.06% copper was absorbed in cellulose when cellulose was treated with 1.0% Cu-MEA solution. However, when cellulose was oxidized and carboxylic acid groups were introduced into cellulose, copper absorption increased and the EPR spectrum in Figure 5.11 confirmed the presence of copper. EPR spectrum shows a similar $A_{\parallel}$ and $g_{\parallel}$ to those obtained in treated wood, suggesting the interactions between copper amine complex and carboxylic groups.

5.6 Discussion

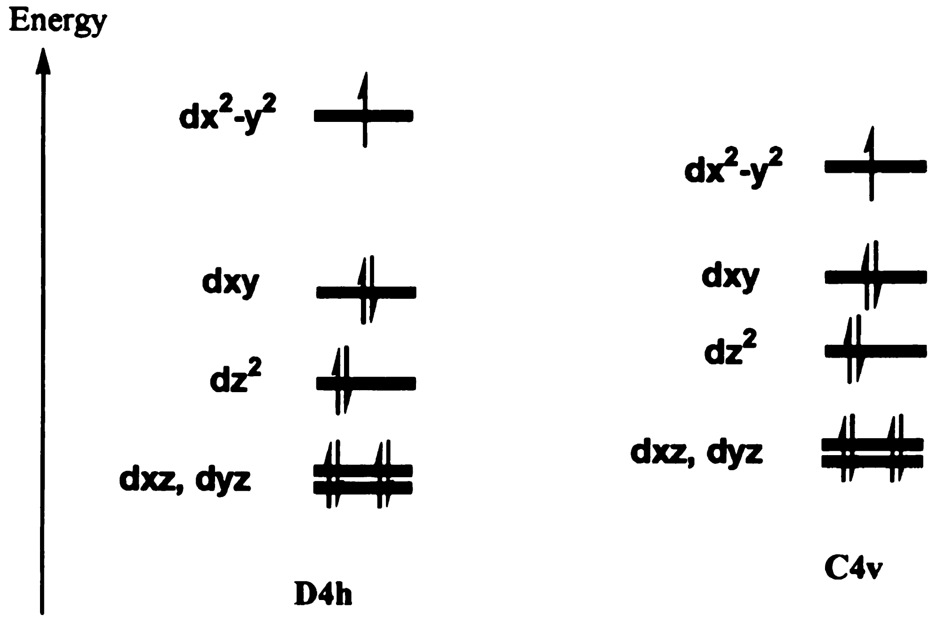
Important information that the EPR spectra yield is the nature of the electronic ground state of Cu^{2+}. A distinction between a ground state dx^2-y^2 and dz^2 lies in that dz^2 is indicated by a low g-value (<2.04), while dx^2-y^2 by an axial spectrum with G > 4.0 (Hathaway and Billing, 1970). The EPR parameters (Table 5.2) and the axial spectra (Figure 5.1 to 5.11) are typical for the copper complexes with a dx^2-y^2 ground state. The axial symmetry of copper complexes with a lowest g-value > 2.04 is usually consistent with elongated tetragonal-octahedral (C4v), square-coplanar (D4h) or square-based pyramidal stereochemistry (C4v) (Hathaway and Tomlinson, 1970). The energy diagrams for these complexes are illustrated in Figure 5.12 (Addison *et al.*, 1978). With such a diagram, the EPR g-factors in axial symmetry can be calculated by the following equations according to "magic pentagon"(Drago, 1997):

$$g_z = g_{\parallel} = 2.0023 - \frac{8\lambda}{E_{xy} - E_{x^2-y^2}}$$

$$g_x = g_y = g_{\perp} = 2.0023 - \frac{2\lambda}{E_{dx^2-y^2} - E_{dxz}}$$

Where λ has a value of –829 cm^{-1} for Cu(II), $g_{\parallel}$ involves a promotion of an electron from ground state dx^2-y^2 orbital to *dxy* orbital (Figure 5.12). Since λ is negative, it gives $g_{\parallel}$ a

Figure 5.12 Orbital energy diagram for Cu (II) complexes



larger value than the g value for a free electron, 2.0023. $g_\perp$ involves a transition of an electron from orbital dx^2-y^2 to orbital dxz (Figure 5.12). The energy needed for this transition is very large so that the second term in $g_\perp$ is going to be very small. Therefore, unlike $g_{||}$, $g_\perp$ does not deviate significantly from the g value of the free electron. Our data agrees with these theoretical calculations well.

Peisach and Blumberg (1974) pointed out that the ligands of copper complexes with axial symmetry are arranged in a environment about the metal ion with four ligands lying in an approximate plane including the copper ion. The ligands are close to the metal center and thus strongly bonded. The other ligands are arranged on a straight line including the Cu^{2+} and perpendicular to the plane. Those ligands perpendicular to the plane usually play only a minor role in both magnetic and optical properties of the copper complex. So, the magnetic properties of copper complexes are governed by the four equatorial atoms, which are bonded to metal center closely.

It has been reported that Cu^{2+} forms chelating complexes with ethanolamine in aqueous solution where two amine ligands chelate one cupric ion center (CuN2O2) (Tauler and Casassas, 1986; Davis and Patel, 1968 and Casassas *et al.*, 1989). The value of $g_{||}$ and $A_{||}$ of copper complexes in the treating solution are 2.263 and 17.1 mK, respectively. These values are in agreement with other CuN2O2 complexes reported in literature (Freyberg *et al.*, 1977 and Xie *et al.*, 1995). The $g_{||}$ and $A_{||}$ values of copper amine treated wood given in Table 5.2 are similar to those of copper complex in aqueous solution and those reported in literature (Freyberg *et al.*, 1977 and Xie *et al.*, 1995). From these g and A values, the chemical interaction between copper amine and wood can be suggested. In the previous chapter, several alternatives have been proposed for copper amine-wood interaction as illustrated in Figure 2.8. If copper amine ligand-exchanges with wood as proposed in Figure 2.8a, the copper amine complex will change form from CuN2O2 in solution to CuN1O3 in treated wood. Nitrogen is more electron-rich than oxygen. Replacement of N by O should reduce the values of $A_{||}$ and increase the values of $g_{||}$. In an extensive review on EPR analysis of copper complexes, Peisach and Bluberg (1974) demonstrated that CuN2O2 has a $g_{||}$ value of 2.2-2.3 and an A-value of 16-20 mK, while $g_{||}$ for CuN1O3 and CuO4 range in 2.3-2.4 and $A_{||}$ less than 16mK. In the current study, copper complexes in solution and Cu-EA treated wood show a g-value of 2.25-2.27 and an A-value of 17.0-18.0 mK except for copper amine treated lignin, which suggests that copper complexes in treated wood are in the form of CuN2O2. The correlation of $A_{||}$ and $g_{||}$ is shown in Figure 5.13. Other CuN2O2 complex systems give the similar relationship between $A_{||}$ and $g_{||}$ (Peisach and Bluberg, 1974). This eliminates the alternative of ligand exchange with the formation of CuN1O3 and supports the hypothesis that the wood acts as the ligands which complex with copper metal center perpendicularly without displacing the amine ligands (Figure 2.8b).

When wood is treated with copper amine, carboxylic groups and phenolic hydroxyl groups can complex with copper amine from perpendicular direction as suggested by Figure 2.8b. Depending on the pH of the system, one or two ligands can attach to the copper center. If two ligands attach to copper amine, a tetragonal-octahedral complex will be formed. If one ligand is added to copper amine, a tetragonal-pyramidal configuration will be formed. The introduction of only one ligand does not change the EPR parameters significantly because A and g are mainly determined by the four equatorial atoms (Peisach and Blumberg, 1974).

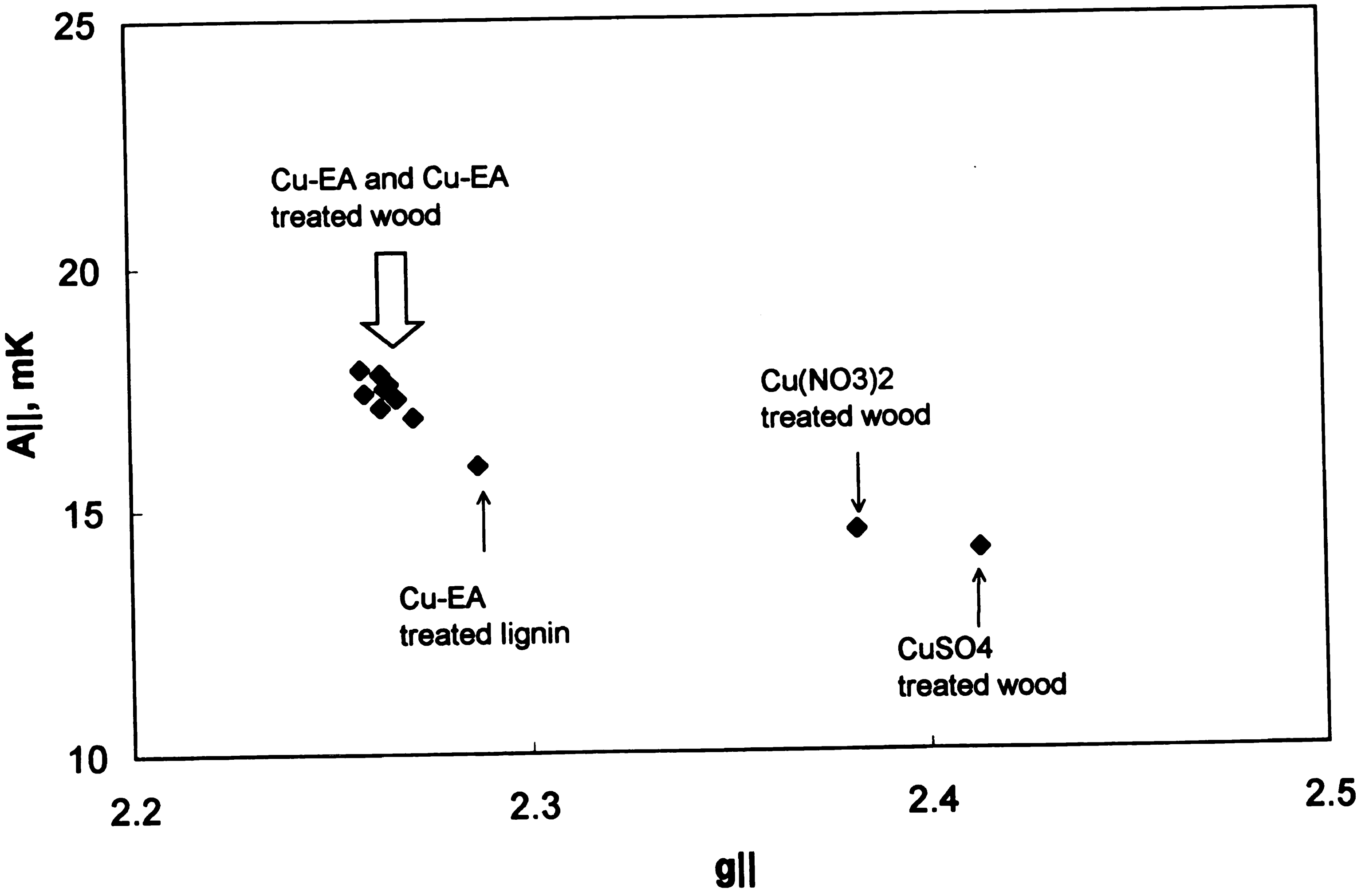


Figure 5.13 Correlation of A|| and g||

5.7 Conclusions

The stereo-structure of copper complexes formed in copper amine treated wood was characterized by EPR. The axial spectra and the electronic parameters determined by EPR suggest that copper amine interacts with wood to form a tetragonal-based octahedral or square-based pyramidal complex when wood is treated with copper amine solution.

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Chapter 6

X-Ray Diffraction (XRD) and X-Ray Photoelectron Spectroscopic (XPS) Characterization of Copper-Amine Treated Wood Substrates

6.1 Abstract

Copper amine treated wood samples were characterized by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). XRD analysis demonstrated that copper amine treatment did not alter the crystalline lattice structure of cellulose. Post treatment steaming of copper amine treated wood causes the formation of a new crystal that was identified as cuprous oxide by XRD. XPS survey spectrum indicated the presence of C1s, O1s, Cu2p and N1s in copper amine treated wood. XPS analysis showed that the oxidation state of copper in treated wood is in cupric form.

6.2 Introduction

X-ray diffraction and X-ray photoelectron spectroscopy techniques have been widely employed to elucidate the nature of copper in treated wood in the area of wood chemistry. XRD is a useful tool for investigating the compounds with ordered structure. It can be used to identify and semi-quantify crystalline compounds present in a matrix. Creely *et al.* (1978) used XRD to study the complexes of cellulose with secondary diamines. In wood protection, Gallacher *et al.* (1995) used XRD to identify copper dimethyldithiocarbamate (CDDC) crystal formation in CDDC treated wood. Sutter *et al.*

(1983) used XRD to confirm the formation of copper oxalate in wood treated with a copper-based preservative.

X-ray photoelectron spectroscopy (XPS), also referred as electron spectroscopy for chemical analysis (ESCA), has been used widely for surface analysis in physical chemistry. Ostmeyer and Elder (1988) applied XPS to examine the reaction of CCA with southern pine. By using ESCA analysis, Williams and Feist (1984) investigated the reactions occurring in wood and cellulose surface after treatment with aqueous chromium trioxide, and proposed that chromic acid was fixed to both wood and pure cellulose.

In the current study, XRD and XPS were used to monitor the change of copper and wood in terms of crystal formation, valency state of copper or redox reaction after copper amine treatment.

6.3 Materials and Methods

6.3.1 Treatment

Defect-free 5 by 10 by 180cm (2 by 4 inch by 6 feet) kiln-dried sapwood boards of southern pine (SP) were used in this study. Cubes measuring 19mm (0.75 inch) were prepared from these boards and stored in a conditioning room maintained at 65% relative humidity (RH) and 20 °C (68 °F) until they reached an equilibrium moisture content (EMC) of 12 ± 3%. The conditioned cubes were then pressure-treated with copper amine (Cu-EA) solutions. The elemental copper content in the solutions was 1.0% by weight. The treating procedure included an initial vacuum at 84.6 kPa for 5 minutes, followed by a pressure level of 690kPa (100 psi) for 1hour, and then a final vacuum for 10 minutes. Treated samples were conditioned at room temperature for 2 weeks before further test.

6.3.2 X-ray Diffractometry

XRD diffraction patterns were obtained on a Rigaku Rotaflex model CN-4148B2 X-ray diffractometer using Cu-Kα radiation (λ= 1.5418Å). The X-ray diffraction was operated at 45kV and 100 mA. Diffraction patterns were collected using DD and DS slot widths of 0.5°. The diffraction angle (2θ) was measured from 5° to 65° at speed of 2°/minute.

6.3.3 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy was operated on a Perkin-Elmer Electronics ESCA 5400 spectrometer. The spectrometer was run at 300 watts, using Mg-K standard PHI 04-548 and an Al K toroidal monochromatic source PHI 10-410. The experiments were performed at a pass energy of 89.45 eV for survey scans and 35.7 eV for high resolution scans.

The wood samples were microtomed into thin slices (about 120 μm) and freeze dried prior to introduction into the spectrometer. The samples were mounted to the sample stubs using double-sided tape and placed into the analysis chamber. Analysis included the collection of a low resolution, wide window survey from 0 to 1100 eV to identify the elements detectable on the surface, followed by a high resolution analysis of 15 to 20 eV in width.

6.4 Results and Discussion

6.4.1 X-ray Diffraction (XRD) Analysis

The XRD patterns of wood and the air-dried treated samples are illustrated in Figure 6.1. The characteristic peaks of cellulose I resulted from the 101, $10\bar{1}$, 002 and

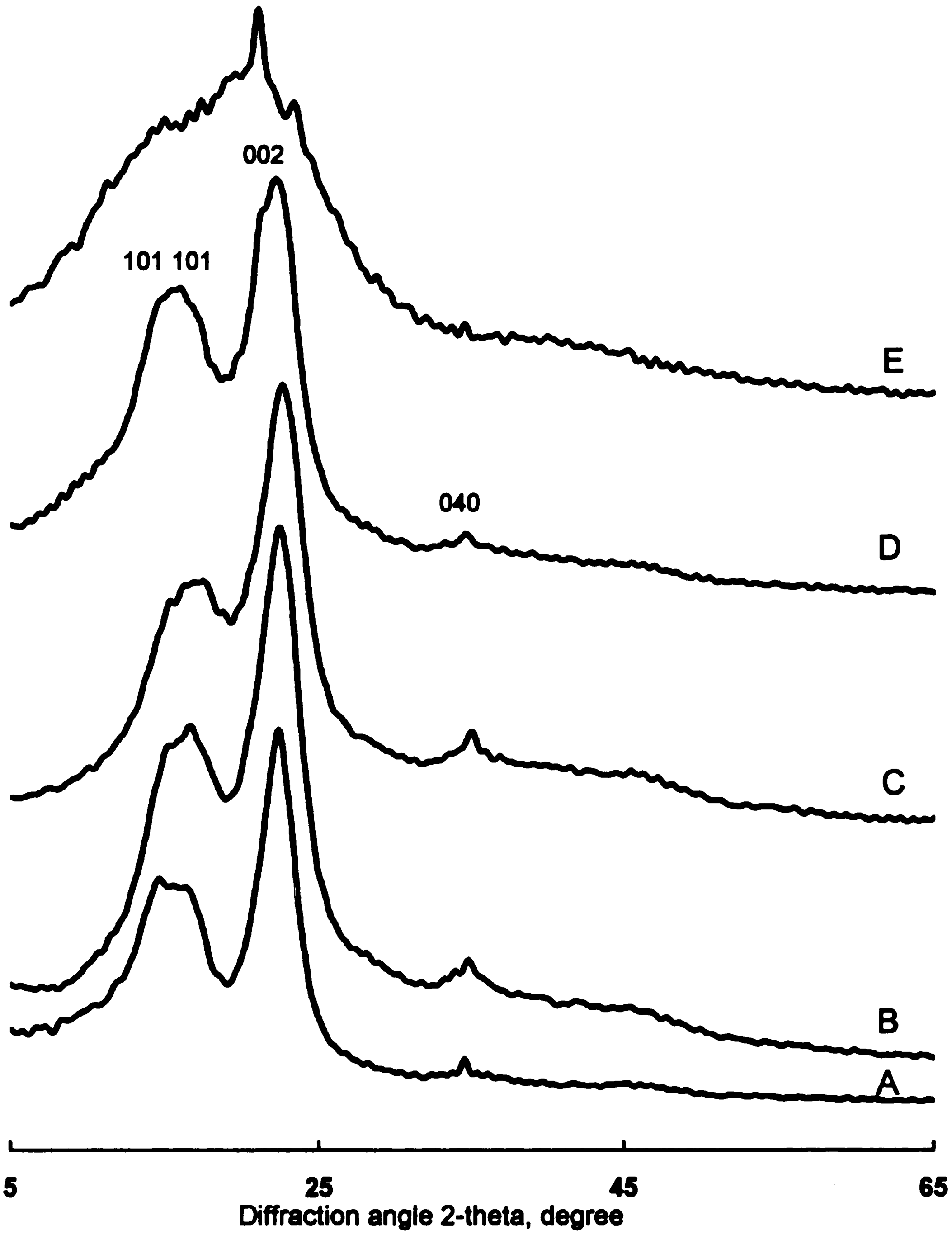

Figure 6.1 XRD patterns of (A). Untreated wood; (B). Cu-MEA treated wood; (C). Cu-MeEA treated wood; (D). Cu-DMeEA treated wood and (E). Cu-MEA treated lignin

040 reflections are present in all samples except lignin. The XRD patterns of copper amine treated wood in Figures 6.1B, 6.1C and 6.1D are similar to that of untreated wood in Figure 6.1A with respect to the crystal lattice type. The pressure treatment with copper amine preservatives did not change or affect cellulose crystal lattice structure.

In wood preservation area, post treatment steaming is usually used to accelerate the fixation of copper-based preservatives in treated wood (Barnes, 1985; Anderson, 1990). Figure 6.2 shows the XRD patterns of post treatment steamed samples. No significant modification in XRD patterns was noticeable after post treatment steaming of wood and lignin (Figure 6.2). However, new peaks appeared in the XRD patterns of Cu-EA treated samples after post treatment steaming (Figure 6.2), suggesting the formation of new crystal(s). The positions of the new peaks are located at 2θ value of 36.5° and 42.1°. The crystal detected in the post treatment steamed Cu-EA treated samples were identified as cuprous oxide (Cu_2O) (Kamdem *et al.*, 1998).

The initial oxidation state of copper in Cu-EA treating solution is Cu^{2+}. The oxidation state of copper in Cu_2O formed during post treatment steaming of Cu-EA treated wood is Cu^{1+}. This suggests that post treatment steaming may promote the reduction of cupric into cuprous. It is well known that wood contains reducing agents, such as aldehyde groups and reducing hemiacetal groups at the end of cellulose chains, which are capable of reacting with Cu^{2+} to form Cu_2O as suggested in Equation 6.1 under a certain condition, such as the steaming conditioning. Since no Cu_2O signal was observed in XRD pattern of Cu-EA treated lignin after post treatment steaming (Figure 6.2E), the redox reaction may occur mainly between carbohydrate and copper.

$$R\text{-}CHO + 2Cu^{2+} + 2H_2O \longrightarrow R\text{-}COOH + Cu_2O + 4H^{+} \quad \text{Equation (6.1)}$$

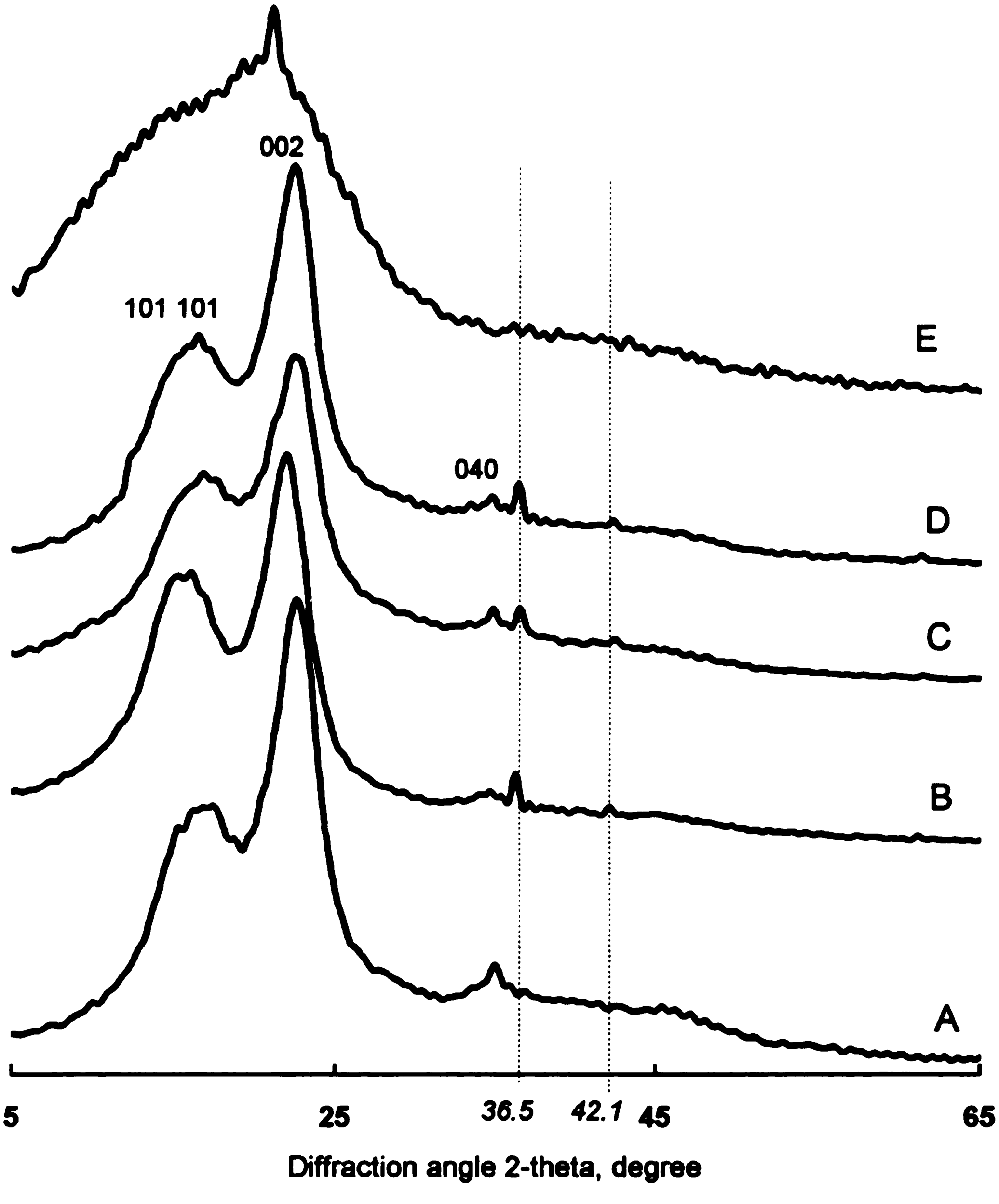

Figure 6.2 XRD patterns of post-steamed (A). Untreated wood; (B).Cu-MEA treated wood; (C). Cu-MeEA treated wood; (D). Cu-DMeEA treated wood and (E). Cu-MEA treated lignin

6.4.2 X-ray Photoelectron Spectroscopic (XPS) Analysis

The surface composition of the specimens can be readily obtained from XPS survey spectra (Figure 6.3). The XPS spectrum of untreated wood shows the presence of C1s and O1s (Figure 6.3A), while the spectrum of Cu-MEA treated wood reveals the presence of C1s, O1s, Cu2p and N1s (Figure 6.3B). The XPS Cu2p spectra are illustrated in Figure 6.4. Cu2p XPS spectra contain two peaks with an energy difference of 20.0eV, one at binding energy (BE) of 952.5eV corresponding to $Cu2p_{1/2}$ and the other at BE of 932.5eV corresponding to $Cu2p_{3/2}$. These data agree with those previously reported (Kamdem *et al.*, 1996). The copper oxidation state is reflected by the BE of $Cu2p_{3/2}$ and the energy difference between $Cu2p_{1/2}$ and $Cu2p_{3/2}$. The oxidation state of copper in Cu-MEA treated wood and in CuSO4 treated wood is similar due to the same Cu2p BE and energy difference between $Cu2p_{1/2}$ and $Cu2p_{3/2}$ (Figure 6.4A and 6.4B). The difference between these two peaks varies from 19.8eV for Cu^0 metal to 20.0eV for Cu^{2+} species (Moulder *et al.*, 1992). XPS data suggests that the oxidation state of copper in both Cu-EA and CuSO4 treated wood is 2+.

The XPS analysis of individual elements in wood and treated wood is given in Table 6.1. Table 6.1 shows that only the moiety of nitrogen and no copper are present in untreated wood. After treatment with Cu-EA, the nitrogen content in wood increased significantly. The leaching of treated sample caused very small percentage loss of nitrogen and copper, suggesting that most of nitrogen and copper are bonded to wood. With an amine free system, such as $CuSO_4$ treated wood, leaching leads to a higher percent loss of copper compared to Cu-EA treated wood. These findings confirm the importance of amine in the formulation of copper amine based preservatives.

Figure 6.3 XPS survey spectra of (A). Untreated wood and (B). Cu-MEA treated wood

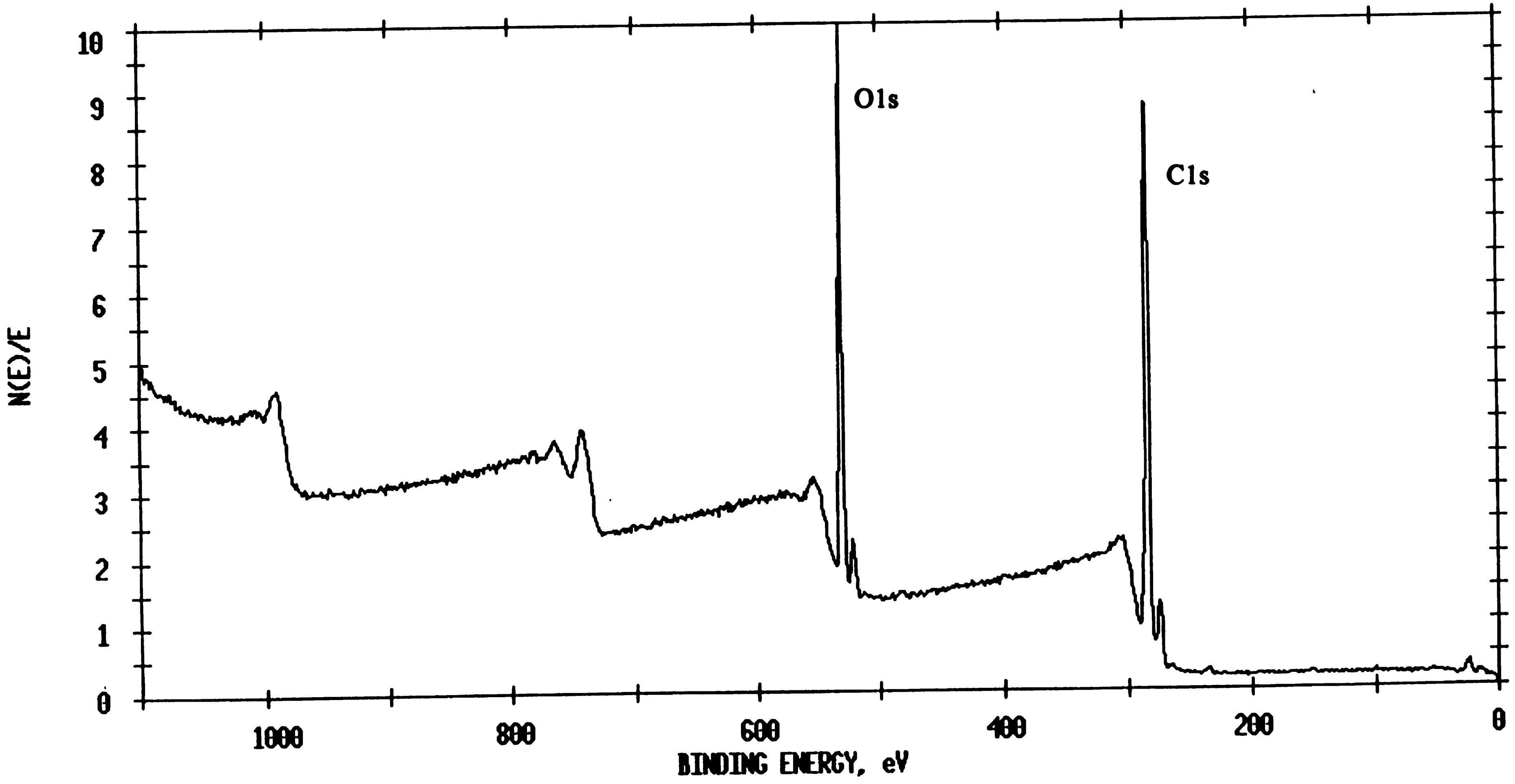
N(E)/E
10
9
8
7
6
5
4
3
2
1
0
O1s
C1s
1000
800
600
400
200
0
BINDING ENERGY, eV

Figure 6.3A

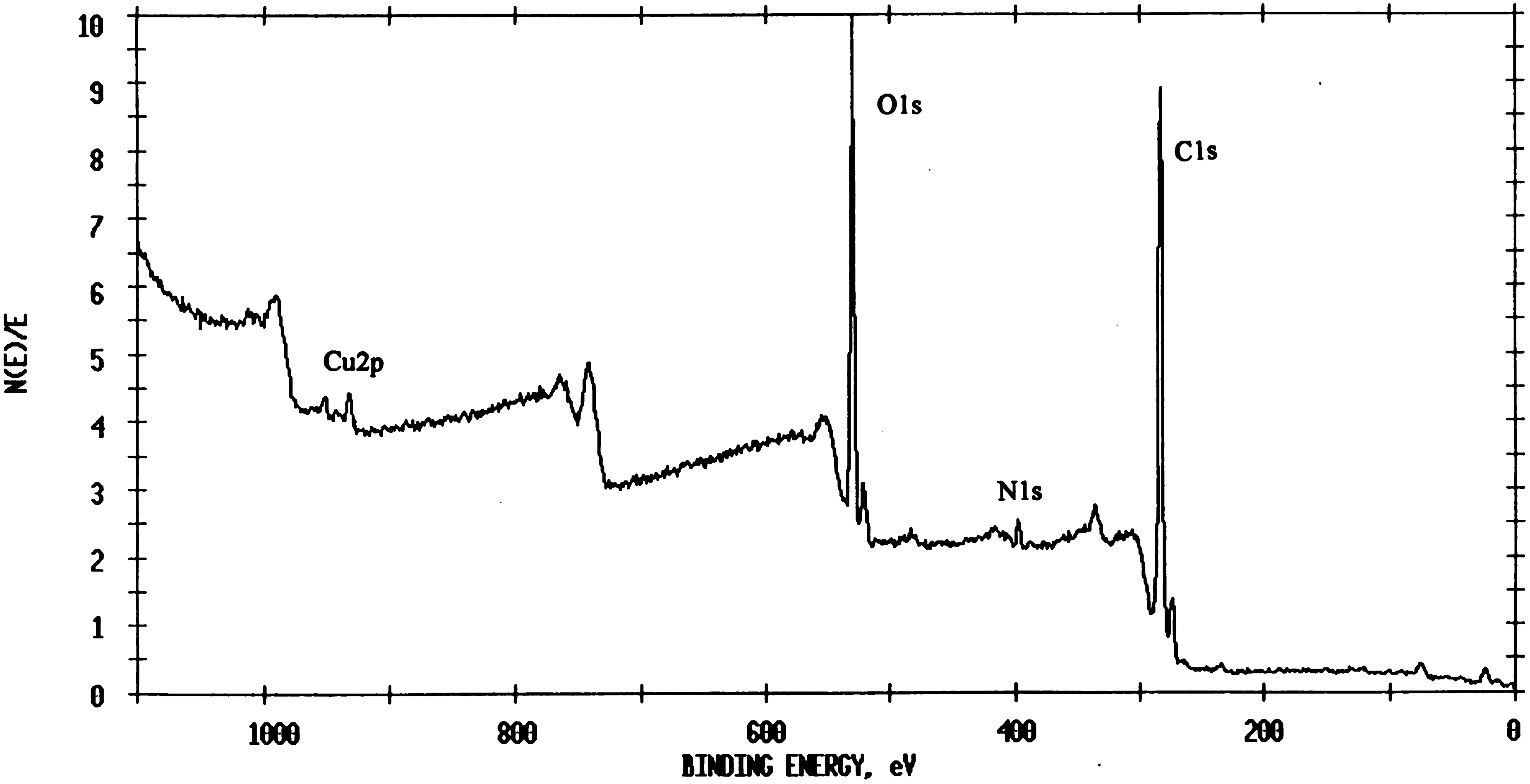
N(E)/E
10
9
8
7
6
5
4
3
2
1
0
O1s
C1s
Cu2p
N1s
1000
800
600
400
200
0
BINDING ENERGY, eV

Figure 6.3B

Figure 6.4 XPS Cu2p spectra of (A). CuSO4 treated wood and (B). Cu-MEA treated wood

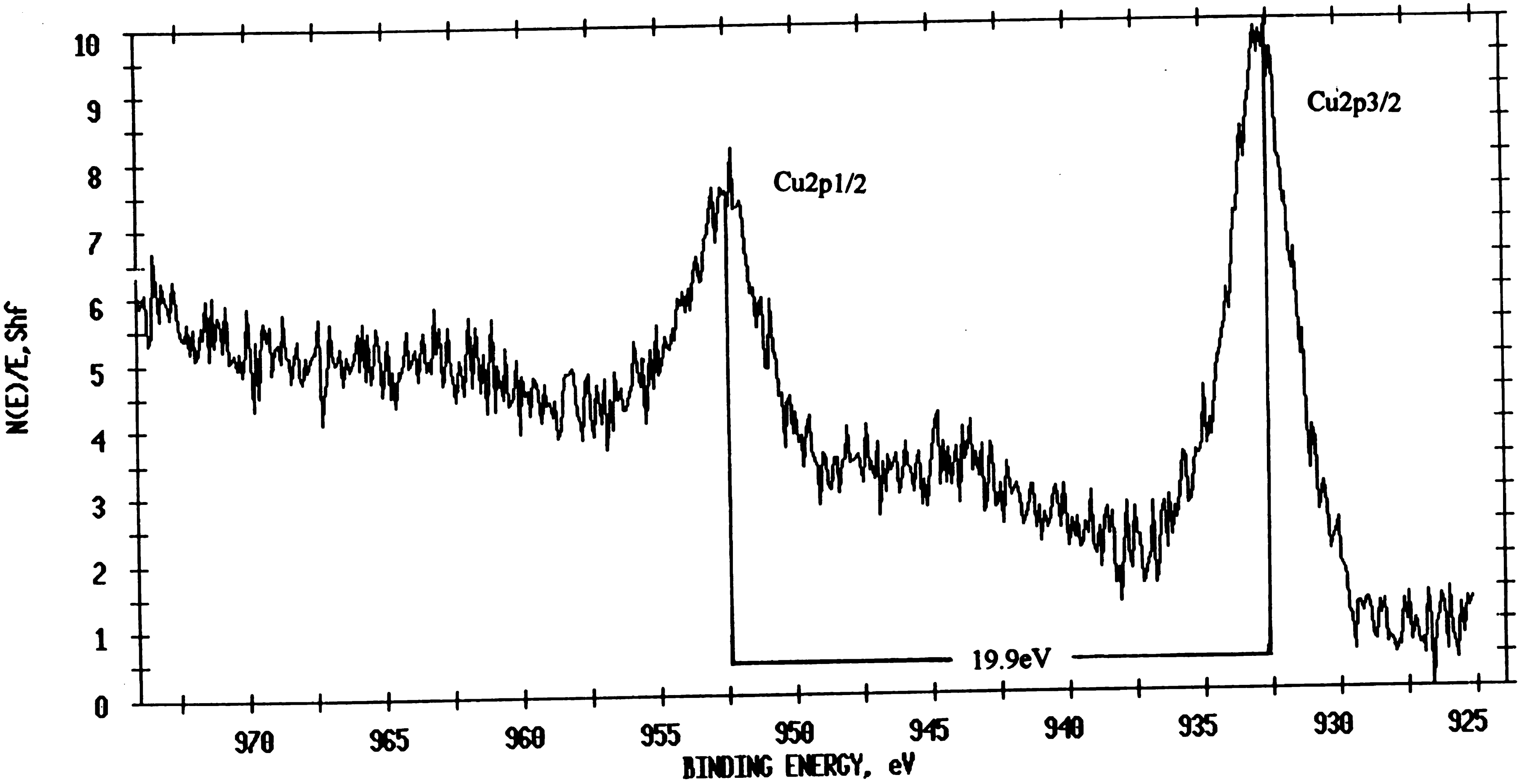
N(E)/E, Shf
0
1
2
3
4
5
6
7
8
9
10
Cu2p1/2
Cu2p3/2
19.9eV
970
965
960
955
950
945
940
935
930
925
BINDING ENERGY, eV

Figure 6.4A

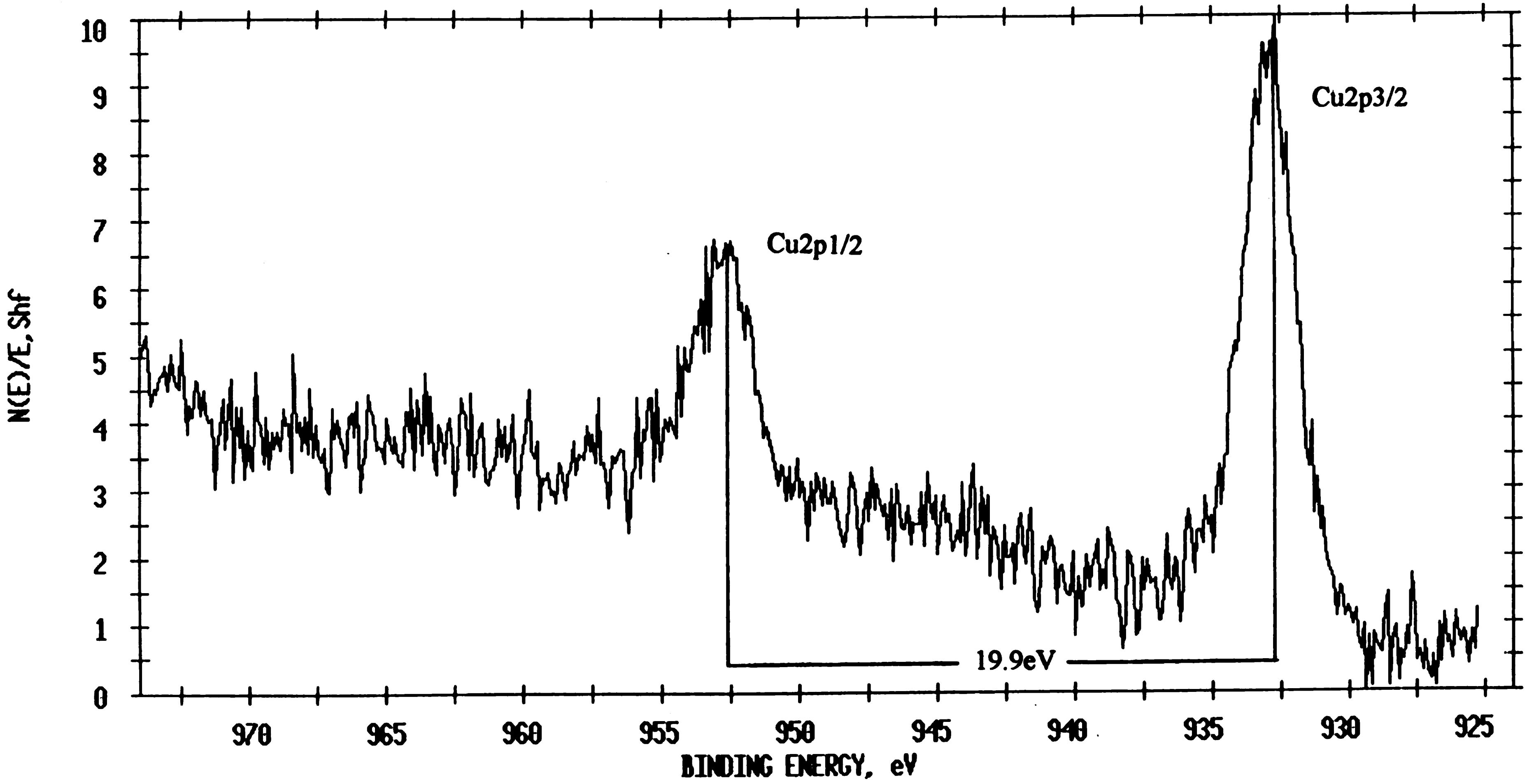
10
9
8
7
6
5
4
3
2
1
0
N(E)/E, Shf
Cu2p1/2
Cu2p3/2
19.9eV
970
965
960
955
950
945
940
935
930
925
BINDING ENERGY, eV

Figure 6.4B

Table 6.1 Atomic composition in the surface of wood and treated wood by ESCA analysis

Wood samples	C, %	O, %	Cu, %	N, %	O/C	
Untreated	72.74	26.85		0.41	0.37	
Cu-MEA treated	68.35	29.45	0.85	1.34	0.43	Unleached
pH = 10.8	69.37	28.74	0.78	1.11	0.41	Leached
Cu-DMEA treated	68.38	29.52	1.00	1.11	0.43	Unleached
pH = 10.9	70.61	27.49	0.94	0.96	0.42	Leached
Cu-DMeEA treated	67.37	30.29	1.18	1.16	0.45	Unleached
pH = 10.6	70.43	27.56	1.07	0.95	0.41	Leached
$CuSO_4$ treated	73.77	25.15	0.70	0.38	0.36	Unleached
pH = 4.1	74.40	24.92	0.29	0.39	0.35	Leached

6.5 Conclusions

1). Cu-EA treatment did not alter the crystal lattice structure of cellulose in wood.

2). Post treatment steaming caused the redox reaction between Cu^{2+} and reducing agents in wood, which resulted in the formation of Cu_2O. The reducing agents are mainly from cellulose and/or hemicellulose.

3). XPS survey spectrum indicated the presence of C1s, O1s, Cu2p and N1s in copper amine treated wood. XPS Cu2p spectra revealed that the oxidation state of copper in treated wood was Cu(II).

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Chapter 7

Conclusions

In this research, the effects of copper source, amine ligand and amine to copper molar ratio on copper retention and leaching of copper amine (Cu-EA) treated wood were investigated. The roles of individual wood components in copper absorption during copper amine treatment and the copper bonding sites in wood were also examined. The Cu-EA treated wood and wood components were characterized by spectroscopic methods. As a result, proposals were given for interactions between wood and copper amine preservatives and the copper fixation mechanism.

The copper retention and leaching of Cu-EA treated wood were influenced by the formulation of copper amine complexes. Stable copper amine complexes can improve copper penetration into wood and therefore increase the retention of copper in treated wood. However, stable copper amine complexes would retard the chemical interaction between the complexes and wood and consequently reduce the copper leaching resistance. Less stable copper amine complexes tend to interact with wood readily and increase the leaching resistance of copper. However, the fast interaction will block the further penetration of copper amine treating solution and accordingly lower the copper retention.

In general, three major factors, namely, pH of treating solution, amine ligand and amine to copper molar ratio, can affect the stability of copper amine complexes. High pH results in deprotonation of copper amine complexes and increases the stability of the complexes. The copper complex of a primary amine (MEA) is more stable than those of either a secondary amine (DMEA) or a tertiary amine (DMeEA) due to the steric hindrance of the methyl groups in DMEA and DMeEA. Increasing the molar ratio of amine to copper can increase the pH of the treating solution and the stability of copper amine complexes. As a general rule, in formulating a copper amine treating solution, the pH, amine ligand, and amine to metal ratio should be taken into consideration and balanced to improve copper retention while minimizing the copper loss during leaching.

Studies of copper absorption on wood components showed that hemicellulose and lignin in wood played significant roles in absorbing copper. Tests with the model compounds of hemicellulose and lignin confirmed that hemicellulose and lignin were the main copper absorption sites in wood during Cu-EA treatment. The role of cellulose in retaining copper was negligible, which is reflected by minimal copper absorbed on cellulose. Removal of extractives from wood also decreased the amount of copper absorbed.

FTIR spectra indicated that carboxylic acid groups in hemicellulose were the major reaction sites for copper. Ester groups in wood, which can be hydrolyzed into carboxylic acid groups through alkaline hydrolysis, behaved similarly to the carboxylic acid groups. These ester groups also provided reaction sites for copper. FTIR analysis of Cu-EA treated holocellulose and Cu-EA treated oxidized cellulose verified the chemical interactions between copper and carboxylic acid groups in wood. In addition, phenolic hydroxyl groups in lignin provided another potential bonding sites for copper during current treating conditions. Aliphatic hydroxyl groups in wood appeared to be inert to react with copper during copper amine treatment.

After Cu-EA treatment, the oxidation state of copper in treated wood is cupric (Cu^{2+}), which was confirmed by XPS. XPS analysis also indicated the presence of C1s, O1s, Cu2p and N1s in treated wood. After leaching, the majority of copper and nitrogen were still retained in wood. XRD investigation demonstrated that Cu-EA treatment did not change the crystalline lattice structure of cellulose in wood. No redox reactions between copper and wood were observed by XRD except when the treated wood samples were post-steamed. Post-steaming of treated samples resulted in the formation of cuprous oxide (Cu_2O) due to the occurrence of redox reaction between cupric copper (Cu^{2+}) and reducing groups in wood, such as aldehyde groups.

The structure of copper complexes in copper amine treated wood was elucidated by the application of electron paramagnetic resonance spectroscopy. Anisotropic axial spectra were observed for all treated samples irrespective of the copper amine formulations. The axial spectra and EPR parameters of all samples indicated that the stereo-structure of copper complexes in copper amine treated wood was tetragonal-based octahedral with a symmetry of C4v or square-based pyramidal with a symmetry of D4h. The interactions of wood with copper amine were through complexation reaction in which functional groups from wood, such as carboxylic acid groups and phenolic hydroxyl groups, complexed with copper amine from perpendicular direction. The copper complexes in both treating solution and treated wood were in the form of CuN2O2 in the equatorial plane of the complexes.

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