FIXATION CHEMISTRY OF AMINE-COPPER PRESERVATIVES

by

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Abstract

The principal objective of this thesis was to study the fixation mechanism of amine-copper preservatives, with an additional focus on the active component HDO (N-cyclohexyl-diazeniumdioxide) in Wolman CX™, to determine its influences on the fixation of the copper.

The degree of fixation was assessed first by a leaching study. The depletion of copper and amine from copper-amine and copper-HDO amine treated Scots pine *(Pinus sylvestris)* blocks was investigated. For copper-amine treated blocks, the greatest leaching resistance was found for copper-monoethanolamine and copper-polyimine treatments, with more than 80% (water leaching) and 50% (buffer leaching) copper retained. Copper ethylenediamine showed the greatest leachability. The inclusion of HDO greatly improved the leaching resistance of the treated blocks to citrate buffer solution, with the copper-HDO diamine system having the highest leaching resistance. The formation of very stable $Cu(HDO)_2$ (bis-(N-cyclohexyldiazeniumdioxy)-copper) precipitate accounted for the enhanced leachability. It was found that about 25-40% of the amine reacted with wood irreversibly and that this was independent of the amine-copper reaction. The residual amine to copper mole ratio retained confirmed the formation of a copper-amine complex in wood. However, whether copper is present as copper(amine).wood or copper$(amine)_2$.wood could not be determined from the leaching study.

The fixation reactions which took place between amine, copper-amine, copper-HDO amine and wood were explored using Fourier Transformed Infrared Spectroscopy

(FTIR), X-ray photoelectron spectroscopy (XPS), and electron spin resonance (ESR). The FTIR spectra revealed that the carboxylic acid and phenolic hydroxyl groups in wood react with both amine solvent and copper to form stable complexes. The FTIR spectra suggested that amine acid salts could be formed and this was supported by the XPS, which also identified that a second amine reaction occurred with phenolic hydroxyl groups in wood. The type of amine copper complexes formed in wood were identified by XPS and ESR. It was found that in copper-amine treated wood, $Cu(amine)_2$.wood was the dominant copper complex. However, in copper-HDO amine treated wood, copper was preferentially formed as $Cu(HDO)_2$ precipitate.

The fixation mechanism of copper and amine in wood was also studied individually through the reactions of vanillin (a lignin model compound), organosolv lignin, Scots pine holocellulose, pectin and extractives with copper amine and copper-HDO amine solution. The reddish copper complex formed from the reaction of vanillin and copper ethylenediamine sulphate was identified by FTIR, ESR and X-ray single crystallography as $Cu(vanillin)_2(H_2O)_2$. In this complex, the methoxyl and water oxygen atoms were coordinated to copper, together with the phenolic oxygen atoms forming a six member coordinated complex. This study suggested that a similar reaction between ethylenediamine copper solution and lignin in wood could take place to form a stable lignin-copper complex without nitrogen present. However, based on the leaching study, XPS and ESR spectra, such reaction would be considered to be a minor reaction in the fixation mechanism of copper amine treated wood. The reactions of copper-amine or copper-HDO amine with organosolv lignin, holocellulose, and extractives confirmed that

these three wood components took an important role in the fixation of copper and amine in wood. The carboxylic acid group in hemicellulose, and the phenolic hydroxyl group in lignin and extractives were the major reactive sites for copper and amine.

The distribution and location of copper in copper amine and copper-HDO amine treated wood was studied using light visible microscopy and scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDX). From the light microscopic study of thin sections of southern pine (*Pinus sp.*) and Douglas-fir (*Pseudotsuga menziesii*), it was found that copper was concentrated in the highly lignified cell corners and compound middle lamella, due to the copper-lignin fixation reaction. For copper-HDO amine treatment, copper was principally observed to deposit on the surface of the cell walls. This implied the preferential formation of a copper precipitate in wood. The observation of crystalline copper solids in ray cells and pits in CuHDO-en treated samples suggested by SEM-EDX the formation of $Cu(HDO)_2$ precipitate in wood. No such deposits were found in copper-amine treated samples.

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List of Abbreviations

AA	atomic absorption spectrometer
ACA	ammoniacal copper arsenate
ACQ	ammoniacal copper quaternary
AmCC	ammoniacal copper citrate
ACZA	ammoniacal copper zinc arsenate
AEEAH	aminoethylethanolamine
CCA	chromate copper arsenate
CDDC	copper dimethyl dithiocarbamate
Cu-AEEA	copper aminoethylethanolamine
CuAZ	copper azole
Cu-en	copper ethylenediamine
Cu-DAP	copper diaminopropane
Cu-MEA	copper monoethanolamine
Cu-Polyim	copper polyethylen imine
$Cu(HDO)_2$	bis-(N-cyclohexyldiazeniumdioxy)-copper
CuHDO-AEEA	copper-HDO aminoethylethanolamine
CuHDO-en	copper-HDO ethylenediamine
CuHDO-DAP	copper-HDO diaminopropane
CuHDO-MEA	copper-HDO monoethanolamine
CuHDO-Polyim	copper-HDO polyethylen imine
DAP	1,3 diaminopropane
DDAC	didecyldimethylammonium chloride
DMSO	dimethylsulphoxide
EDX	energy dispersive X-ray analyzer
en	ethylenediamine
ESR	electron spin resonance spectroscopy
FTIR	Fourier transform infrared spectroscopy
HDO	N-cyclohexyl-diazeniumdioxide
HPLC	high performance liquid chromatography

KBr	potassium bromide
KHDO	N-cyclohexyldiazeniumdioxy potassium
MEAH	monoethanolamine
Polyim	polyethylen imine
SEM	scaning electon microscopy
TLC	thin layer chromatography
UV-Vis	ultraviolet visible photo- spectroscopy
XPS	X-ray photoelectronic spectroscopy

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Chapter 1

Background

1.1. Introduction

Wood, as a renewable source, is used extensively in the world, and the demand for wood supply is continuing to grow with the increase of the population in the world. However, wood, in many traditional uses, is being replaced by other structural materials such as steel, concrete, aluminum and synthetic polymers. It is not difficult to see that in most of the cases, the change from wood to an alternative material has been made in the hope of obtaining a longer service life for the product and/or a lower maintenance cost during its lifetime. For wood, to compete against these alternative materials, its susceptibility to biological attack must be eliminated. This can usually be achieved through the use of an effective wood preservative and treating procedure (Ruddick, 1980).

In fact, the wood preservation industry has provided a very positive way to sustain the natural forest source. By extending the life of wood products far beyond the natural durability of the wood, the wood preservation industry acts as a major contributor to improving the environment, in terms of maintaining the nation's forest. In 1998, the wood industries in Canada produced a total value of 28.6 billion dollars, of which almost 1.4% was generated by the wood preservation industry. Today, the production of treated lumber in North America is estimated to be about 215 million m^3/yr (Canadian Industry

Statistics Development Team, 2000). When reviewing the development of the wood preservation industry in regard to the end-use products from its birth to today, profound changes have occurred. The wood preservation business has shifted from being primarily a producer of treated wood products for the utility industries (crossties, piles, and poles) to being predominantly a producer of treated lumber for use in building construction, manifesting itself most clearly in the use of treated wood for decks (Preston, 2000). This paradigm shift in the wood preservation industry resulted in a dramatic consumption of waterborne wood preservatives, because of their ease of application, low cost, and the pleasant appearance of the wood after treatment (Hulme, 1979).

However, the wood preservation industry is coming under increasing pressure as a negative influence on the environment in spite of its positive contribution to protect our forest. The major concern, regarding the process of treating wood, is the loss of chemicals in service, and perhaps of greatest importance, the ultimate disposal of the treated wood when its service life is over. These concerns have motivated the wood preservation industry to develop alternative preservatives, which should be more friendly to the environment, and easier to dispose of. Recently, copper-amine preservatives, which are free of chromium and arsenic, are developing as one of the future directions.

1.2. Development of ammoniacal and amine-copper preservatives

Most of the consumer lumber was treated with chromated copper arsenate (CCA), the most widely used preservative in North America (Micklewright, 1998). It now also accounts for almost half of the treated poles produced in Canada. The performance of permeable softwood, treated with CCA, has proved to be an outstanding success story for wood preservation. CCA has achieved this dominant position because of three characteristics: a) being a very effective preservative; b) being fixed to the wood following treatment, and c) leaving the surface of the treated wood free of surface deposit.

Ammoniacal copper wood preservatives have been known since the beginning of the twentieth century. One of the first to be introduced was Aczol in 1907, an ammoniacal solution of copper and zinc salts with phenol (Hunt and Garratt, 1963). In 1925 the University of California set out to develop a wood preservative that could fix itself in the wood, prevent biological deterioration, and leave the wood surface clean and safe to handle. The product was later patented and named Chemonite™ (Gordon, 1940). It comprised of copper salts as fungicide, and arsenic salts as insecticides, dissolved in aqueous ammonia. Upon evaporation of the ammonia, water-insoluble copper arsenate was precipitated. Ammoniacal copper arsenate preservative (ACA) was submitted to the AWPA Preservatives Committee for standardisation in 1949 (Baechler, 1949). The first commercial Chemonite™ treating plant was built in 1935 to preserve lumber, ties, poles, and piles, mainly of white fir (*Abies concolor*). Later, in 1941, a Chemonite™ treating

plant was built that processed almost exclusively coastal Douglas-fir (*Pseudotsuga menziesii*) (Fritz, 1947).

Industry concern with leaching of arsenic from ACA treated wood led to replacement of some (fifty percent) of the arsenic. Ammoniacal copper zinc arsenate (ACZA) was first accepted by the Canadian Standards Association for wood preservation in 1989. The replacement of some of the arsenic by zinc did not appear to reduce its effectiveness against decay fungi (Wilcox, 1987), but did improve the resistance to leaching (Rak, 1976). Subsequently a similar ACZA formulation was introduced in the United States in 1981 in which the Cu:Zn:As ratio was 1:1:1 (Best and Coleman, 1981). In 1983 the AWPA included the 1:1:1 formulation of ACZA in the preservative standard (Morgan, 1989). During the past two decades, there has been growing resistance by the general public and government agencies in Europe, North America and Japan to the use of chromium and arsenic containing preservatives. Ammonia-copper based preservatives, therefore, face the challenge of further development if they are to be evolved into more environmentally friendly wood preservatives. Most of the formulations which have been developed since the later part of the 1970s use copper as the active cation because of its excellent fungicidal action.

Recently, ammoniacal copper citrate (AmCC) and ammoniacal copper/quaternary ammonium compound formulations (ACQ) have been developed which exhibit relatively low mammalian toxicity and low environmental impact (Findlay and Richardson, 1983). AmCC was presented to the AWPA Preservatives Committee for standardisation in 1984. The field tests of the AmCC treated stakes showed promising results, and confirmed that

a ratio of 2:1 copper to citrate was the optimal formulation (Osmose Wood Pres. Inc., 1993). Sundman (1984) and Archer *et. al.* (1993) reported that ACQ appeared to provide similar protection at equivalent preservative retentions of active ingredients to CCA. A study by Preston *et. al.* in 1985 focused on ammoniacal copper carboxylates, and examined various fatty acids across a range of stoichiometric ratios of cation to anion. Extensive biological testing with ammoniacal copper octanoate showed that this system has considerable potential for use as a ground contact ammoniacal preservative.

Although the ammoniacal copper preservative was developed over 50 years ago, and was commercialized in the 1960's, it has not achieved a significant status, despite providing an enhanced penetration in the heartwood of refractory species, such as Douglas-fir (*Pseudotsuga menziesii*), spruce (*Picea* sp), or lodgepole pine (*Pinus contorta*). The principal reason for this resistance is that the evaporation of the volatile ammonia during drying of the treated timber leads to the formation of water insoluble copper salts on the surface of treated wood. This is undesirable when the treated wood is used in residential construction, where the appearance is the major consideration. An alternative approach which may solve this problem is to solubilize the copper in an amine. This approach has been adopted by several manufactures to produce novel preservatives, notably, Wolman CX™ (Dr. Wolman GmbH), ACQ type D (CSI), and Copper Azole (Hicksons).

ACQ type D is a direct development from ACQ type B, retaining the same active ingredients (quaternary ammonium compound and copper component), the same ratio of active ingredients, and provides equivalent performance characteristics. The difference

between ACQ-B and ACQ-D lies in the solvating system, the ammonia in ACQ-B being substituted by short chain alkanolamines/amines. This change allows easier treating practices, easier handling charateristics of the treated wood, and lower treatment operational costs. Furthermore, wood treated with ACQ-D provides more uniformity of color. All of these improvements are achieved while retaining the same excellent performance reported for ACQ-B (CSI, 1994).

Wolman CX™, an amine copper preservative, is a chromium and arsenic free wood preservative based on $Cu(HDO)_2$ and boric acid. $Cu(HDO)_2$ possesses excellent fungicidal efficacy, with high stability, low water-solubility, low toxicity, and favourable environmental behavior. It is the principal component in Wolman CX™ formulations. Tests have shown that the biological efficacy of Wolman CX™ was superior to the usual salts (Dr. Wolman GmbH, 1990).

Copper Azole (CuAz) preservative, another amine preservative system, has been formulated for use by commercial pressure treating plants and the treated wood may be used in both high and low decay hazard environments. The products have good fixation properties of two of the active components: copper and a highly effective triazole biocide. The triazole biocide in this formulation is tebuconazole. Extensive tests (Fox et. al., 1994) have shown that even after leaching and outdoor weathering, the preservative is effective against a wide range of wood destroying organisms, including copper tolerant fungi. Moreover, the CuAz preservative has excellent ancillary properties. The treated wood has an even green color with a clean surface appearance and no odor. Wood treated

with CuAz has strength, resistance to corrosion, and conductivity properties, similar to that of untreated wood (Fox, *et. al.,* 1994).

1.3. Objectives

With increasing pressure on arsenic and chromium containing wood preservatives, the wood preservation industry has focused on copper amine preservative formulations with considerable promise for further development for heavy-duty wood preservatives. However, relatively little is known about the fixation of these alternative preservatives. In order to maximize the opportunities of these alternatives, the NSERC/Industry Chair in Wood Preservation developed a research program which focused on the fixation chemistry of copper-amine system.

The principal objective of this research is to study the fixation chemistry of amine-copper preservatives, with particular focus on Wolman CX™ to determine the effects of the amine and co-biocide HDO on the fixation, leachability and effectiveness. It will be supported by three sub-objectives, which are:

1. To determine the influence of selected amines on the fixation chemistry of copper preservatives in softwood.
2. To examine the reactions which take place between copper and the wood components as well as solid wood, understand the dominant fixation mechanism of copper-amine preservatives in wood.
3. To investigate the influence of HDO on chemical fixation reactions in the Wolman CX™ formulation.

The research findings will be an important step in providing the foundation for further research on formulated preservatives. For example, formulations with different amines will be expected to behave differently, since the stability of the amine-copper complexes are expected to be amine specific. Research on different amines will allow new formulations with enhanced fixation to be developed. Overall, understanding the interactions between preservative chemicals and wood components are important to the development of effective wood preservatives and fixation technologies. The development of such knowledge remains a fertile research area, and vital importance as the environmental pressures on the existing preservatives continue to grow.

Chapter 2

Literature Review

2.1. *In situ* instrumental analysis techniques

The chemical interaction between wood preservatives and wood components is not well understood, mostly due to the complex nature of wood. Several analytical techniques, such as Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and electron spin resonance spectroscopy (ESR), have proved to be particularly helpful and provide a valuable insight into the reactions which occur in wood during fixation (Craciun et. al., 1997; Craciun and Kamdem, 1997; Dagarin et. al. 1996; Hughes et. al. 1994; Humar and Petric, 2000; Kaldas and Cooper, 1998; Kamdem and Zhang, 2000; Ostmeyer et. al., 1988; Pohleven et. al. 1994; Ruddick et. al., 1993; Yamamoto and Ruddick, 1993; Zhang and Kamdem, 2000). In this review of preservative fixation studies, these three nondestructive, solid-state, spectroscopic techniques were utilized to elucidate the nature of the wood and chemical interaction, in an attempt to understand the influence of treatments on the properties of treated wood. These methods are not predicated on an extraction or isolation step, and may, therefore, provide a better indication of the actual bonding of the copper in the wood.

2.1.1. FTIR spectral analysis of treated wood

The FTIR spectrum is obtained by passing a beam of infrared radiation of constantly varying frequency through a sample of the compound. A detector generates a

plot of percent transmission of radiation vs. the wavenumber that is transmitted. The bonds in the irradiated molecules are constantly vibrating. A stretch is a vibration occurring along the axis of the bond, while a bending vibration does not occur along the line of the bond. Each stretching and bending vibration of a bond is associated with a certain frequency. When a chemical is irradiated with an energy that exactly matches the energy required to the vibration frequency of one of its bonds, the vibrating bond will absorb energy to generate an absorption peak in the FTIR spectrum. The wavenumber range of interest lies between 4000 cm^{-1} to 400 cm^{-1}. The functional group region (4000 cm^{-1} to 1000 cm^{-1}) generally contains absorptions due to bond stretches as they require more energy and thus a higher frequency. The fingerprint region (1000 cm^{-1} to 400 cm^{-1}) contains many complex signals generally resulting from bond bending that are unique for each compound.

FTIR has been successfully employed to characterize the chemical interactions between wood components and copper preservatives. Thin wood sections can be used directly in FTIR analysis (Liu and Ruddick, 1993; Liu, et. al. 1994; Jiang and Ruddick, 1999). The functional groups in treated and untreated wood can be evaluated without altering the nature of the sample during preparation, so that the reactions between preservative components and the constituents of wood might be detected.

FTIR was applied in the analysis of CCA treated southern pine by Ostmeyer et. al. in 1989. It was found that the CCA treatment resulted in a decrease in both the aromatic and carbonyl peaks of the infrared spectra. Single or double component treatments had no marked effect on the aromatic or carbonyl groups compared to water treated or untreated

controls. It was suggested that all three of the CCA components are required in the treating solution for wood/CCA reactions to occur. Michell (1993) used FTIR to study the reaction of wood and of lignin model compounds with chromium trioxide and concluded that CrO_3 reacts with wood via the aromatic ring of lignin.

FTIR has also been successful in providing considerable information during the weathering process (Hon et al. 1982; Hon, 1988; Jin et. al., 1991; Evans et. al., 1992; Liu and Ruddick, 1993; Liu, et. al., 1994; Zhang and Kamdem, 2000b). Liu and Ruddick (1993) studied the weathering of DDAC (didecyldimethylammonium chloride) treated wood by FTIR. The structural changes in lignin, due to the fixation of DDAC, could be also monitored by FTIR. They found that DDAC treatment caused the lignin band at 1510 cm^{-1} to split and decrease in intensity. The weathering study indicated that DDAC treatment accelerated the weathering of wood mainly via degradation of lignin. FTIR spectra of the weathered samples confirmed that removal of lignin and formation of carbonyl groups was greater for DDAC treated samples than untreated controls. The influence of ACQ treatment, especially the presence of copper(II), on wood weathering was investigated using FTIR by Liu et. al. (1994). This study demonstrated the effectiveness of ammoniacal copper in a quats formulation to protect wood from weathering. The FTIR revealed that the ACQ treatment slowed wood photodegradation, mainly via inhibiting the formation of carbonyls and delignification during weathering. Recently, FTIR was employed in the study of weathering of copper-amine treated wood to monitor the chemical changes in the functional groups on the wood surface (Zhang and Kamdem, 2000b). It was found from FTIR spectra that copper-amine treatment can retard

the photodegradation of wood, probably due to the interaction of copper-amine and the phenolic hydroxyl group so as to limit the lignin degradation.

The interest of many researchers in the field of fixation chemistry of wood preservatives is focused on the identification of absorption sites of copper and amine in wood. FTIR is a useful technique which can provide a valuable insight into the interactions between chemicals and wood. The chemical changes in the FTIR spectra of copper naphthenate treated wood were observed by Craciun and Kamdem (1997). They suggested that the interaction between wood and the active component from copper naphthenate occurred through a ligand exchange process including R–COO^- sites from wood hemicellulose. The application of FTIR to copper dimethyl dithiocarbamate (CDDC) treated wood revealed that wood and copper-complex interaction took place partially through a ligand exchange reaction between wood carboxyl groups and 2-ethanolamine of the copper complex (Craciun and Kamdem, 1997). FTIR was also used in the study of the characterization of copper ethanolamine treated wood by Zhang and Kamdem (2000) to determine and monitor the alterations in wood and wood components, treated with a copper-amine solution. This research strongly suggested that the carboxylic groups in hemicellulose and the phenolic hydroxyl and ester groups in lignin are the major bonding sites for copper. However, the role of the amine in the fixation reaction was not identified in their study. Research by Jiang and Ruddick (2000) employed FTIR to study the fixation reaction of copper ethylenediamine and wood. It was found that both ethylenediamine and copper ethylenediamine treatment caused the loss of the carboxylic acid functionality. This highlighted the important role of amine in the fixation reaction of

copper amine in wood. The same observation was found in the FTIR spectra of ethanolamine treated wood by Humar and Petric (2000).

2.1.2. The principle of XPS technique

X-ray photoelectron spectroscopy (XPS) is one of the most effective and sensitive surface analysis techniques providing information on both the oxidation state and type of bonding present for a specific chemical element (Christie, 1990; Ruddick, 1992b, and Ruddick et. al., 1993). In XPS the sample surface is irradiated with a monochromatic source of x-rays, causing photo-ionization of atoms in the sample. The resulting photo-emission is observed by measuring the energy spectrum of the photoelectrons produced during the analysis. For each atom in a molecule, there will be valence electrons associated with chemical bonding present in the molecule, as well as core electrons not directly associated with the bonding. The binding energy of these core electrons is unique for each atom and can be used to fingerprint the atoms present in the sample. Siegbahn *et. al.* in 1967 discovered that the binding energy of an atom's core electrons were not fixed but were influenced by the chemical environment. The changes in the screening by the core electrons can give rise to small shifts in the binding energy. These 'chemical shifts' allow changes in the chemical environment around the atom to be studied.

For carbon based polymers such as cellulose and lignin, Dorris and Gray (1978) have interpreted the C(1s) spectra in terms of: C1 type carbons bonded to other carbons or hydrogen, (C-C, C-H or C=C); C2 type carbons corresponding to C-O bonding; C3 type carbons bonded to two oxygen atoms (HO-C-OH) or to a carbonyl group (C=O), and

C4 type carbons bonded in a carboxylic structure (O-C=O). Thus XPS C(1s) spectra of wood reflect the various types of carbon present in lignin, holocellulose and extractives. The C1 component of C(1s) arises predominately from the lignin and extractive constituents of wood. The C2 component of the XPS spectra of wood, in which the carbon atoms are bound to a single non-carbonyl oxygen, arises from mainly the carbohydrate component, although lignin also contributes a small amount. The C3 component can come from holocellulose and lignin, and C4 is mainly from hemicellulose in wood.

2.1.3. XPS spectral analysis of copper and nitrogen

There have been few reports about the XPS measurements of copper compounds. Frost et. al. (1972) extensively researched copper compounds using XPS. Almost all of the commercially available simple cuprous and cupric compounds were examined. The presence of satellite peaks was defined as a characteristic peak for the cupric compounds. Novakov (1971) studied the XPS spectra of five copper compounds, and reported the existence of satellites of 2p bands even in the cuprous compounds like CuCl and Cu_2O. Frost et. al. (1972) suggested that the satellites in the XPS spectra recorded by Novakov (1971) arose from surface contamination of the cupric species. The chemical shifts of the copper atoms as well as the atoms in the ligands were found to be dependent not only on the oxidation state but also on the kind and number of ligand atoms. The effects of the lattice energy and the release of the anions overwhelmed that of the donation of electrons from the ligand molecules (Frost et. al., 1972).

XPS has been widely used to evaluate the surface of wood treated with the copper based wood preservatives (Ostmeyer, 1988; Ruddick, 1992b, Ruddick et. al., 1993; Yamamoto and Ruddick, 1993; Kaldas and Cooper, 1993; Craciun et. al., 1997; Craciun and Kamdem, 1997; Jiang and Ruddick, 1999). In all CCA, CDDC, copper naphthenane, and copper ethylenediamine treated wood, the $Cu(2p_{3/2})$ and $Cu(2p_{1/2})$ spectra exhibited a satellite peak at high binding energy, confirming the presence of copper (II) complexes during the fixation of copper (Frost *et. al.*, 1972; Kaldas and Cooper, 1993; Craciun et. al., 1997; Craciun and Kamdem, 1997; Jiang and Ruddick, 1999). However, for CCA treatment, the longer CCA soaking time (3 hr.) resulted in oxidation of the originally formed Cu(I) compounds with binding energy of 933.9 eV (Kaldas and Cooper, 1993). It was suggested that the reduction of Cu(II) to Cu(I) was affected by organic free radicals formed during the oxidation of CCA treated wood.

The XPS spectra recorded at ambient temperature showed that the copper-amine compounds both in pure form, as well as in treated wood, were relatively easily reduced with the formation of copper(I) during spectral analysis. However, there was no evidence that this was occurring during fixation (Jiang and Ruddick, 1999). Frost et. al. (1972) also reported the readily reduction of copper(II) compounds during XPS measurement.

An extensive series of nitrogen compounds was studied by Nordberg et. al. (1967), in which the chemical shifts of the nitrogen 1s-level correlated with the charge on the nitrogen atom were investigated. The binding energies for the 1s electrons in nitrogen in a wide range of nitrogen containing compounds comprising inorganic and organic salts, as well as neutral molecules of various sizes, were examined by XPS (Nordberg et.

al. 1967). The spectra obtained from compounds which contained several equivalent nitrogen atoms gave spectra showing only one peak, while compounds which contained non-equivalent nitrogen atoms, gave spectra with more than one peak (Nordberg et. al., 1967; Jiang and Ruddick, 1999). The binding energy of nitrogen in free amine was reported to be 398.1 eV, and for the amine acid salt 401.0 eV. Nordberg et. al. (1967) explained that, although no rigorous theory exists for the dependence of binding energies of electrons in inner shells on chemical bonding, the results supported the idea that the shifts in the binding energy, determined by XPS, reflect the charge distribution in molecules, and can be used for the study of structural problems, which are connected with the charge distribution. Nitrogen 1s electron spectra were recorded for five rhenium dinitrogen complexes by Folkesson in 1973. He found that the nitrogen 1s electrons of coordinated dinitrogen gave rise to two peaks. It was evident that the electronic structure around the two nitrogen atoms was different, as the difference in N1s binding energy of the two nitrogen atoms corresponded to different effective charges on the nitrogen atoms. The N1s spectra of pure solid copper diethylenediamine nitrate ($[Cu(en)_2(NO_3)_2]$), as well as copper ethylenediamine treated wood, were examined by Jiang and Ruddick (1999). The N1s spectrum of $[Cu(en)_2(NO_3)_2]$ showed two well resolved single peaks at 400.36 eV and 407.2 eV associated with the nitrogen present in amine and nitrate respectively. The nitrogen XPS spectra of copper ethylenediamine treated wood suggested that the amine was bound to copper as well as reacting with wood. Craciun and Kamdem (1997) also applied XPS to the wood treated by copper naphthenate-ethanolamine solution.

However, N1s was not clearly detected on the treated wood surface by XPS. This was explained by the deep penetration of 2-ethanolamine into the wood cell walls.

2.1.4. The principle of ESR technique

ESR can only be used for studying molecules containing atoms with one or more unpaired electrons. The application of microwave frequency radiation to such atoms, in the presence of an applied magnetic field, causes the atom to absorb electromagnetic energy. This resonance is described by the equation:

$$h\upsilon = g\beta B$$

where: β is the Bohr magnetron constant for the electron
B is the magnetic field
h is Planck's constant
υ is the resonance frequency
g is a proportionality constant which reflects the electron environment of the unpaired electron in the molecule.

For a free electron, g = 2.0023. In a molecule, the unpaired electron can occupy an orbital which is quite well localized on a single atom or it may be delocalised over several atoms. The magnitude of g is then related to the nature of the bonding to the ligand and can be quite different from 2.0023. Only electromagnetic radiation with the frequency (υ) containing the exact amount of energy corresponding to that needed to

produce a transition between the ground and excited energy states of the electron gives an ESR signal.

The unpaired electron, which gives rise the ESR spectrum, is very sensitive to its local surroundings. The nuclei of the atoms in a molecule or complex often have a magnetic moment, which produces a local magnetic field at the electron. The interaction between the unpaired electron and the nuclei in the molecule is called the hyperfine interaction. It gives us a wealth of information about our sample such as the identity and number of atoms which make up a molecule or complex as well as their distances from the unpaired electron. These hyperfine interactions are of equal intensity, separated by the coupling constant 'A'. Therefore, ESR results are usually reported in terms of a spin Hamiltonian and expressed as the 'g' and 'A' tensors. The principal values of 'g' and 'A' in anisotropic spectra yield information about the molecular environment of the unpaired electron responsible for the resonance and the nature of the nuclei with which it interacts.

2.1.5. ESR spectral analysis of copper

Copper(II) is the most common d^9 system, which has been widely studied. The majority of complexes have distorted six-coordinate structures in which two bonds are longer than the remaining four. The unpaired electron is in the $d_{x^2-y^2}$ orbital and all other orbitals are doubly occupied. For copper(II) and its nuclear spin value of I=3/2, the ESR spectrum of Cu(II) compounds will show four equally spaced features (2I+1) due to the hyperfine interaction.

It was first suggested by Kivelson and Neiman (1961) that $g_{//}$ and $A_{//}$ independently vary with the composition of the ligand atoms bound to copper. Vanngard (1972) had compiled $g_{//}$ and $A_{//}$ for a series of model compounds and proteins and suggested that the ESR technique might be employed to define the structure of the copper site in the copper proteins. Peisach and Blumberg (1974) selected a series of copper compounds with different ligands of oxygen and nitrogen atoms to demonstrate how the ESR parameters of $g_{//}$ and $A_{//}$ could be used for the assignment of structure of copper compounds. It was found that the more nitrogen donor atoms bonded to the copper, the smaller values of $g_{//}$ and larger values of $A_{//}$. This is accounted for more electron rich nitrogen. These conclusions were confirmed earlier by Ruddick (1992b), who compiled $g_{//}$ and $A_{//}$ for a series of copper-treated samples and suggested that ESR might be employed to define the geometric relationship of iso-structural copper complexes formed in the treated wood. It was found that complexes with four planar copper-oxygen bonds, *e.g.* $[Cu(H_2O)_4]^{2+}$, had a larger value of $g_{//}$ and a smaller value of $A_{//}$, while the corresponding molecules containing four copper-nitrogen bonds in a plane, such as $[Cu(en)_2]SO_4$, have smaller values of $g_{//}$ and larger values of $A_{//}$. The parameters for copper bound to two nitrogen atoms and two oxygen atoms lie between the two extremes.

Electron spin resonance (ESR) has proved another extremely useful technique for 'in situ' examination of chemical reactions in wood (Plackett et. al., 1987; Hughes, 1992 and 1994; Ruddick *et. al.*, 1994). For CCA or ACA treated wood it is possible to observe an ESR spectrum, since copper (II) compounds are paramagnetic. An early ESR study of CCA treated wood was carried out by Plackett *et. al.* (1987) who studied radiata

pine and extracted lignin impregnated with CCA and copper sulphate. The ESR results revealed that copper sulphate treated radiata pine sapwood samples could provide good quality copper(II) signals at room temperature, and it was suggested that hydrated Cu^{2+} ions were residing in fixed sites within the timber.

More detailed work by Ruddick (1992b) and Hughes *et. al.* (1992) focused on reactions of other copper species in wood, as well as the fixation reaction product found in CCA treated wood. The copper sulphate treated wood exhibited a hyperfine structure at lower field, in which the copper was bonded to four (or six) oxygen atoms in a square planar (or distorted octahedral) configuration. Wood impregnated with copper acetate dissolved in either water or methanol gave similar spectra, which also compared well to that of copper sulphate treated wood. Clearly, in these three treatments any interaction with the wood substrate was independent of the solvent employed (Ruddick 1992b). The copper ESR spectrum of western hemlock, treated with CCA, gave a simple broad ESR spectrum, similar to that produced by $CuSO_4$ solution alone (Ruddick, 1992b).

Identification of ammoniacal copper(II) octanoate in aqueous solutions and its determination in treated wood was carried out by Pohleven et. al. (1994) using ESR. By the comparison of ESR spectra of $CuSO_4$ and Cu(II) octanoate aqueous ammonia solutions, it was concluded that in the Cu(II) octanoate-water-ammonia system, Cu(II) was present as a Cu(II) octanoate-ammonia complex, indicating the active substance in treatment of wood with this solution is a copper(II) octanoate-ammonia complex, rather than the tetra-aminecopper(II) species.

In ammoniacal copper treated wood, the copper ions had a higher $A_{//}$ value and lower $g_{//}$ value than those for the corresponding hexa-aquocopper ion, arising from an increase in the electron density on the copper, since nitrogen is a more electron rich atom than oxygen (Peisach and Blumberg, 1974). This supported the hypothesis that in ammoniacal copper treated wood copper-nitrogen bonded complexes were formed in the wood. Hughes *et. al.* (1992) also found similar electronic parameters after leaching, suggesting that nitrogen still remains attached to the copper. It has been shown that for a copper complex possessing a square planar geometry, there is an inverse dependence of $A_{//}$ on $g_{//}$ (Peisach and Blumberg, 1974). This dependence can help to identify the copper ligand groups in the copper complexes of known structure. Ruddick (1992b) found that ammoniacal copper carbonate treated wood gave ESR spectra in which the $A_{//}$ was slightly smaller and the $g_{//}$ values larger, than those in the original ammoniacal solution. This was interpreted as being consistent with the loss of two ammonia ligands from the tetra-aminecopper complex, present in the solution. In wood these have been replaced by copper-oxygen bonding either from water or from the wood substrate.

2.2. Fixation of copper based preservatives

2.2.1. Fixation of ammoniacal copper preservatives

Even though ammoniacal copper wood preservatives have been known for more than a half century (Hunt and Garratt, 1967), the fixation mechanism is still not well understood. Unlike CCA preservative, the ammonia in the ammoniacal copper system offers an alternative method to fix copper in wood to the oxidation-reduction of chromium which forms the basis for CCA fixation. The use of ammonia allows the solubilisation of insoluble copper compounds in ammonium hydroxide and allows copper to precipitate in wood as the ammonia evaporates.

The fixation mechanism of ammoniacal copper preservatives in wood has been reported by Eadie and Wallace (1962), Clarke and Rak (1974) and Sundman (1984). Following the impregnation of the ammoniacal copper preservative solution into the wood, it has been suggested that tetra-aminecopper ions react by ion exchange with functional groups in the wood, such as carboxylic groups (Kupchinov *et. al.*, 1975). In addition, the evaporation of ammonia causes the break down of the complexes in solution to form water insoluble copper salts, such as copper arsenate in the case ACA (Hartford, 1973).

The generally accepted fixation theory for ammoniacal copper preservatives in wood was challenged as being oversimplistic, when it was observed that ACA treated spruce poles retained an enhanced nitrogen level more than two years after treatment (Ruddick, 1979). An analysis of four zones in ACA treated spruce pole sections was

made: at the surface (0 - 5 mm), at the limit of the copper penetration, the heartwood just beyond the limit of the copper penetration, and the center of the cross section. The results showed that the nitrogen level was greatly enhanced in the ACA-treated wood, and that the nitrogen content appeared to be related to the ACA retention. In addition, there was evidence that the ammonia had penetrated beyond that achieved by the copper, indicating that some nitrogen remained strongly bound in the treated wood. Electron spin resonance (ESR) spectroscopic studies of ammoniacal copper treated wood (Hughes *et. al.* 1994; Ruddick, 1992b) confirmed that the copper-nitrogen complexes were formed in the wood after treatment with ammoniacal copper solution.

In order to better understand the nature of the copper complex formed in wood, reactions of ammoniacal copper solution with vanillin, a lignin model compound, and taxifolin, the principal extractive of Douglas fir heartwood were investigated (Ruddick and Xie, 1994; Xie *et. al.*, 1994). Since lignin is known to possess excellent potential for complexing preservative components such as copper (Butcher and Willsson 1982; Pizzi 1982 and 1990), the initial studies focused on lignin model compounds. Vanillin was used to imitate the abundant guaiacyl units of lignin in wood, to investigate the possible reaction between lignin and ammoniacal copper solutions. (Guaiacyl units constitute 80-90% of the aromatics in soft wood lignin). It was found that ammoniacal copper solution could react with vanillin, to form a stable water-insoluble copper complex. Single crystal x-ray crystallographic studies confirmed that a stable copper-ammonia-vanillin complex $[Cu(vanillin)_2(NH_3)_2]$ was formed (Xie et. al., 1995), in which the ligands are arranged around the Cu(II) in a distorted octahedron. The Cu-O (phenolic oxygen atoms) and the

Cu-N (ammonia nitrogen) formed a square plane around the central copper. The very distorted octahedral configuration is completed by the Cu-O (methoxy oxygen) which are coordinated to the plane containing the phenolic oxygen and ammonia nitrogen atoms and at a greater distance than the in-plane phenolic oxygen. (Xie *et. al.*, 1995). This observation suggested that reactions between ammonia copper and guaiacyl units in lignin are likely to be important.

A second study showed, that while ammoniacal copper solutions reacted with taxifolin in Douglas-fir heartwood to produce a dark black copper-ammonia-taxifolin complex, acidic, neutral or basic copper solutions, or ammonium hydroxide alone were unable to produce the color reaction. Analysis of the copper complex confirmed the presence of nitrogen (Ruddick and Xie, 1994). The formation of such complexes as copper-ammonia-vanillin and copper-ammonia-taxifolin under laboratory conditions, supported the finding of enhanced nitrogen content in ammoniacal copper treated wood in service (Ruddick, 1979).

The knowledge of the reaction mechanism between ammoniacal copper solution and cellulose has been well established. An aqueous solution of tetra-aminecopper hydroxide, $[Cu(NH_3)_4](OH)_2$, is a good solvent for dissolving cellulose, and is widely used for the viscosity determination of pulp in the paper and pulp industry. The tetra-aminecopper hydroxide can swell, peptize, and eventually disperse cellulose. The dispersion of cellulose in cupriammonium hydroxide is accompanied by a chemical reaction. The interaction of the cupric ions in strong ammonium hydroxide solution with glycol-like hydroxyl groups to form complexes, has been reported extensively. Reeves

(1949) suggested that such complex formation was critically dependent on the distance between the hydroxyl groups, on adjacent carbon atoms and the angles between these groups. Hinojosa *et.al.* (1974) studied the interaction of tetra-aminecopper ions with cellulose using ESR. They found that the reaction between tetra-aminecopper ions and cellulose was very rapid and reversible. When the concentration of ammonia was decreased in the cupric ion-ammonium hydroxide-cellulose complexes, the ESR signal due to the paramagnetic resonance of the complex decreased or was lost. It was concluded that the reaction of tetra-amincopper ions with adjacent hydroxyl group on the cellulose to form complexes, depended on an optimum distance between the hydroxyl groups. Evidently, wetting of cellulose fibers with solutions of strong bases allowed the adjacent hydroxyl groups to rotate to favorable positions to yield this optimum arrangement. When the base was removed, rotation of the hydroxyl groups occurred to give less favorable positions for complexing with cupric ions (Hinojosa *et. al.*, 1974).

In addition to reactions with wood components, precipitation reactions of components in a preservative formulation are also important. Clarke and Rak (1974) found that the replacement of a portion of the copper in ammoniacal copper arsenate (ACZA) with zinc, reduced the leachability of the arsenic. The leachability of the arsenic clearly depended on the preservative formulation, although only small amounts of copper or zinc leached from any of the tested formulations (Rak, 1976). Similar results were reported in later studies of ACZA fixation (Lebow and Morrell, 1993), which supported the premise that arsenic immobilization occurred through the formation of insoluble metal-arsenate precipitates. Lebow and Morrell (1995) also showed that the fixation of

ACZA components in wood appeared to occur through both adsorption and precipitation reactions. Arsenic appeared to precipitate in direct proportion to zinc, suggesting the formation of a zinc arsenic compound, while copper, in particular, was readily adsorbed by the lignin and heartwood extractives, which suggested that phenolic groups were primary reaction sites. Zinc also underwent similar adsorption reactions but to a lesser degree. The relative adsorption rate of copper onto the wood components is shown in Figure 2-1 (Lebow and Morrell, 1995). This data confirmed that for the reactions of copper with lignin heartwood, xylan, sapwood and cellulose, the most significant adsorption of copper took place on the lignin, and heartwood extractives.

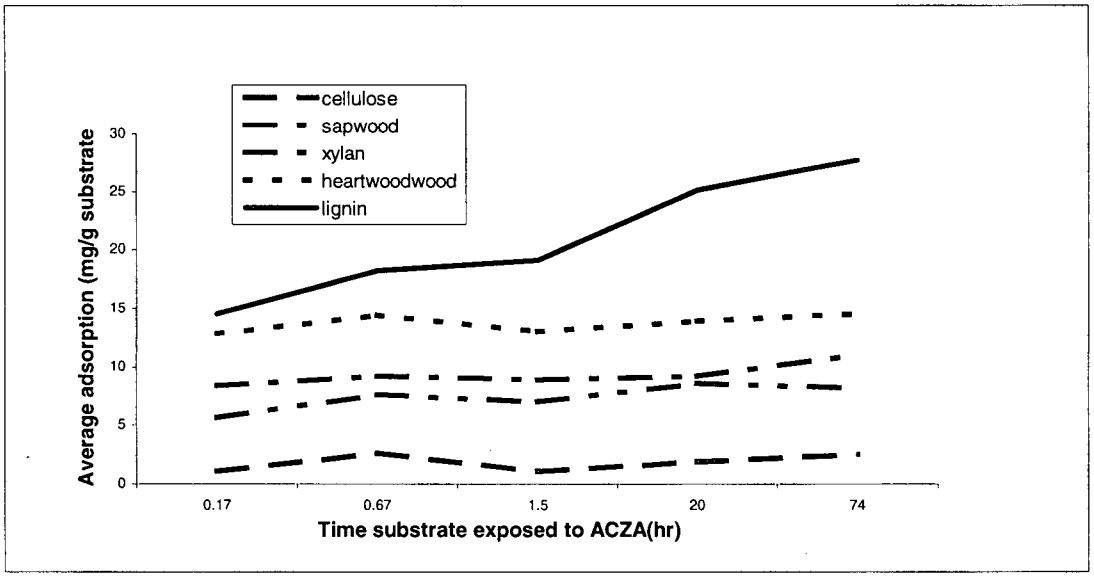


Figure 2-1. Absorption of copper from ACZA solution by wood components (reproduced from Lebow and Morrell, 1995).

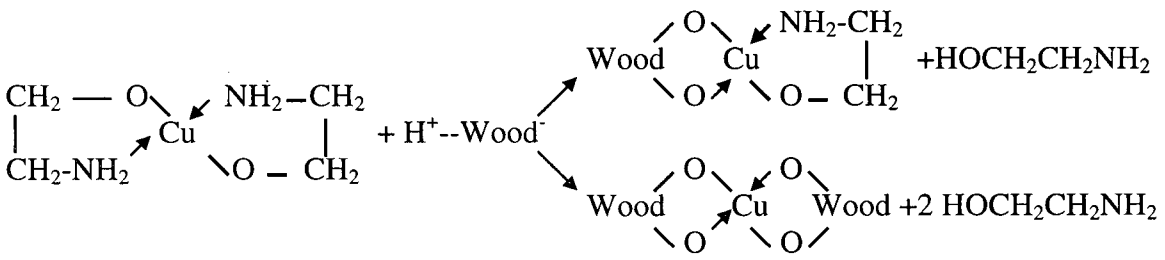
2.2.2. Fixation of amine-copper preservatives

In the ammoniacal copper system, the loss of ammonia from the tetra-aminecopper present in the solution in the wood is rapid and this initiates the fixation reaction. With the ammonia evaporation, there is a stepwise reduction in the number of ammonia molecules bound to copper. This can be described by the below reaction sequence.

$$[Cu(H_2O)_2(NH_3)_4]^{2+} \xrightarrow{-NH_3} [Cu(H_2O)_3(NH_3)_3]^{2+} \xrightarrow{-NH_3} [Cu(H_2O)_4(NH_3)_2]^{2+} \xrightarrow{-NH_3}$$

$$[Cu(H_2O)_5(NH_3)]^{2+} \xrightarrow{-NH_3} [Cu(H_2O)_6]^{2+}$$

For the amine-copper system, the volatility of the amines is much lower. The copper-amine complex formation with wood can not be initiated by loss of ammonia, but by the neutralization of the amine by acid groups in wood. The high pH of the amine solution, will enhance the exchangability of phenolic protons in wood, thereby promoting reaction with the copper. For copper dissolved in monoethanolamime solvent, the fixation reaction with wood may be summarized by the reaction scheme shown below.



It is proposed (CSI report, 1994) that in the amine based ACQ-D preservative, the quaternary ammonium compound fixes in wood a) through ion exchange with anionic active sites, and b) by adsorption at higher concentrations. The same authors assert that the fixation of copper in ACQ-D is through: a) ion exchange reactions between the cupric complex cations and acidic functional groups such as the carboxylic acid groups of lignin and hemicellulose; b) complex formation with cellulose by the hydrogen bonding with hydroxyl or nitrogen groups, or replacement of an amine functionality from the copper ion complex with the hydroxyl ion of cellulose; and c) formation of insoluble copper carbonate salts resulting from the loss of ligand during drying. The FTIR characterization of CDDC treated wood revealed that the interaction of wood and copper amine complex occurs partially through a ligand exchange between carboxylic groups and ethanolamine of the copper complex (Craciun et al., 1997).

Current research has focused on both phenolic and carboxylic functional groups as potential bonding sites for copper. Research by Thomason and Pasek (1997) has reported that selective adsorption of copper and boron from amine copper preservative solution to southern pine sawdust is achieved via two distinct and separate pathways. The authors considered that the difference between the copper retention measured in treated sawdust and that calculated on the basis of solution 'up-take', was due to the adsorbed copper. Adsorbed copper determined in this way was shown to react exclusively with the carboxylic groups found in hemicellulose constituents. In contrast, boron was found to react not with the carboxylic groups, but rather with another wood component (presumed to be lignin) by the formation of borate esters. The mechanism for selective copper

adsorption proposed by Tomason and Pasek (1997) appears to suggest that hemicellulose rather than lignin may be the primary reaction site for copper as found by other researchers (Pizzi, 1982; Xie *et. al.*, 1995; Jiang and Ruddick, 1999; Kamdem and Zhang, 2000; and Zhang and Kamdem, 2000). It is important to note that reactions of copper preservatives in the heterogeneous structure of wood may not be easily simulated using individual model compounds of wood components or sawdust. It is also possible that the assumption that no reaction takes place between wood and the amine-copper solution, except for that accounted for by the difference in the assay and the weight uptake, may be invalid. Reactions between copper solutions and lignin are known to be rapid and significant.

The reaction sites of wood with copper were also studied by Zhang and Kamdem (2000). The interactions between copper ethanolamine and phenolic hydroxyl, carboxylic, and ester groups in wood components were examined by FTIR. It was concluded that hemicellulose and lignin play a significant role in bonding copper in copper ethanolamine treatment, while the role of cellulose in retaining copper was negligible. They found that the carboxylic groups in hemicellulose and the phenolic hydroxyl and ester groups in lignin are the major bonding sites for copper. However, the authors ignored the important interactions between amine in the copper-amine solution and the functional groups in wood such as phenolic hydroxyl, carboxylic groups. It has been shown by FTIR that amine also mainly reacts with the carboxylic groups in hemicellulose and the phenolic hydroxyl in lignin (Humar and Petric, 2000; Jiang and Ruddick, 2000). The effect of wood components on copper adsorption during copper-

amine treatment was investigated by Zhang and Kamdem (2000). It was found that the organosolv lignin took up significantly higher amounts of copper than the other wood substrates. However, this lignin was examined to contain about 4 times as much phenolic hydroxyl groups as the native lignin in softwood. In contrast, cellulose had the least reactive site for copper among the wood substrates. Holocellulose showed a relatively higher copper adsorption. Xylan, as a model compound of hemicellulose, displayed higher copper reactivity than holocellulose. The extractive-free wood showed less copper absorption than unextracted wood (Lebow and Morrell, 1995; Zhang and Kamdem, 2000). This study confirmed the important role of lignin and hemicellulose in the copper adsorption during copper amine treatment. The carboxylic acid groups in hemicellulose and the phenolic hydroxyl in lignin are clearly the major reactive sites for copper.

In order to better understand the nature of the fixation mechanism of copper complexes formed in wood, the reaction of copper ethanolamine solution with a lignin model compound, vanillin was studied by Ruddick et. al. (2000). A green water-insoluble copper complex was formed during reaction, and its structure was characterized by X-ray crystallography, FTIR and ESR. It consisted of a dimer, in which a copper atom was bound to both a vanillin and two ethanolamine molecules. It was suggested by Ruddick et. al. (2000) that when wood is treated with a copper ethanolamine solution, a reaction between lignin and the copper ethanolamine solution occurred to form a stable lignin-copper-ethanolamine complex.

As mentioned in Chapter 1, the industry has developed a number of alkaline copper preservatives, that are based on copper as the primary biocide, solubilized as a

complex. It is usually combined with co-biocides to provide protection against wood destroying fungi. For example, in Wolman CX™ formulation, one of the active ingredients is $Cu(HDO)_2$ (Figure 2-2), in which the bidentate hydroxy-diazeniumoxide ligand coordinates to the copper (II) through its oxygen atoms (Klebe et. al., 1996).

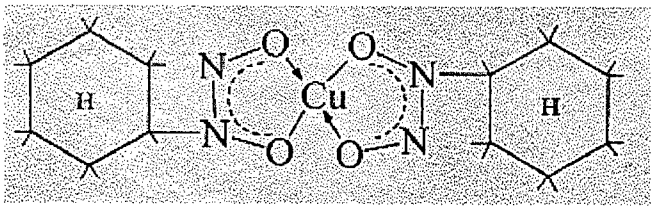


Figure 2-2. The molecular structure of $Cu(HDO)_2$

The precipitation of $Cu(HDO)_2$ during the fixation reactions was suggested to take place through a reduction of the pH value caused by the neutralization with the carboxylic acid groups in wood (Dr. Wolman GmbH, 1990).

In summary, during the fixation of ammoniacal/amine copper preservatives in wood, several reactions have been proposed to take place (Ruddick, 1994). These include the formation of copper complexes with lignin, heartwood extractives, hemicellulose, the precipitation of simple copper compounds in the wood, as well as the formation of simple copper holocellulose or lignin compounds in wood, without ammonia or amines. It is clear that much research is needed before a clear understanding of the fixation chemistry is developed. In particular, the relative importance of complex formation and precipitation reactions, as well as the roles of hemicellulose and lignin, remain unknown.

Research is also needed to determined the primary differences in the fixation mechanism of ammoniacal and amine copper preservatives.

Chapter 3

The leaching resistance of copper-amine and copper-HDO amine in treated Scots pine

3.1. Introduction

The loss of active biocidal components from the treated wood is important for two reasons. Firstly, the degree of protection provided by the preservative declines, and secondly, it impacts on the environmental acceptability of the preservative. For copper based formulations, the amount of copper lost from the treated wood directly correlates to the degree of preservative fixation. A relative assessment of leachability can be determined from laboratory leaching experiments. However, care must be exercised when extending these comparative results, to what might occur under actual service conditions, since the rate of loss in the latter will be much lower or can be much different.

Copper can form very stable complexes with amines (Manriquez et. al., 1996). However, if amine-copper preservatives are to fix in wood, a balance is required between the copper to amine bonding, and that formed between copper and the wood components. If the copper to amine bonding is too strong, the preservative will remain unreacted with the wood, and will tend to leach easily. Zhang and Kamdem (1999) investigated the influence of copper source, amine ligands and amine to copper mole ratio on copper leachability. It was concluded that the leaching of copper was influenced greatly by the formulation of copper amine complexes. High pH formulation systems resulted in lower copper leaching resistance. However, a 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 the leaching resistance of copper (Zhang and Kamdem, 1999).

Previous researchers have shown that during treatment of wood with ammoniacal copper solution, both simple copper precipitates and diammine-copper complexes are formed. The relative importance of both forms of copper on leachability was compared by Jiang and Ruddick (1997). The results confirmed that both forms of copper resisted leaching by distilled water. However, when exposed to the more aggressive leaching conditions, using the sodium citrate buffered solution, the diammine-copper complexes were significantly more resistant to removal from the wood.

$Cu(HDO)_2$ is one of the highly effective ingredients in the Wolman CX™ formulation. The objective of this study was to investigate the leachability of the wood treated by copper-HDO amine and copper amine solutions, and determine the influence of different amines on the fixation of copper in wood. Besides the distilled water leaching, citrate buffer solution was used as a highly aggressive leaching medium. This leaching environment was chosen to provide additional information on the relative stability of amine-copper complexes and simple copper precipitates formed in wood.

3.2. Materials and methods

3.2.1 Leaching experiment of copper-amine treated wood

3.2.1.1 Treating solutions

The copper-amine solutions, including copper monoethanolamine (Cu-MEA), copper ethylenediamine (Cu-en), copper 1,3-diaminopropane (Cu-DAP), copper aminoethylethanolamine (Cu-AEEA), and copper polyethylenimine (mixed with 20% of monoethanolamine) (Cu-Polyim), were supplied by Dr. Wolman GmbH. Their composition is listed in Table 3-1, and the treating concentrations of copper (expressed as CuO), and mole ratio of nitrogen to copper are shown in Table 3-2. Monoenthanolamine (MEAH), ethylenediamine (en) and 1,3-diaminopropane (DAP) were obtained from Fisher Scientific Company and Matheson Coleman & Bell Manufacturing Chemists, respectively, as reagent grade solvents. They were diluted to 5% by weight with distilled water prior to use.

3.2.1.2 Sample preparation

Scots pine (*Pinus sylvestris*) sapwood was used in this study. Oven dried Scots pine blocks (50 x 25 x 15 mm) were placed in a beaker in a desiccator, which was then evacuated for 30 min using a vacuum pump. The vacuum was then used to assist treatment of the blocks with the copper amine or amine solutions. Once atmospheric pressure had been reached, the beakers were removed from the desiccator, and allowed to stand for one hour. The blocks were removed from the treating solutions and air-dried on a wire screen for two weeks at ambient conditions, to ensure completion of fixation.

Table 3-1. The composition of the copper-amine solutions supplied by Dr. Wolman GmbH.

	LP13742a1 (%) Cu-DAP	LP13742b1 (%) Cu-en	LP13742c (%) Cu-MEA	LP13742e (%) Cu-Polyim	LP13742g1 (%) Cu-AEEA
Water	95.87	96.32	42.75	37.25	94.88
1,3 diaminopropane	2.35	---	---	---	---
ethylene diamine	---	1.90	---	---	---
monoethanolamine	---	---	39.50	20.00	---
polyethylenimine	---	---	---	25.00	---
aminoethylethanol-amine	---	---	---	---	3.34
$Cu(OH)_2.CuCO_3$	1.78	1.78	17.75	17.75	1.78

Table 3-2. Concentration and mole ratio of nitrogen to copper in copper-amine treating solutions after dilution.

Solution ID	Cu-MEA	Cu-en	Cu-DAP	Cu-AEEA	Cu-Polyim
Concentration of CuO (%)	1.19	1.10	1.00	1.21	1.22
N:Cu (mole ratio)	4.0:1	3.9:1	4.0:1	4.0:1	3.9:1
Amine:Cu	4:1	~2:1	2:1	2:1	>2:1

Eight blocks were treated with each solution to provide three blocks for leaching in water or citrate buffer, with two blocks being retained for other experiments, such as elemental analysis, light microscopy and scanning electron microscopy.

3.2.1.3 Leaching assessment

During leaching, each block was placed individually in a beaker, and vacuum impregnated with 125 ml of the leaching solution for two hours. The leaching solutions were a) 125 ml of distilled water and b) 125 ml of a sodium citrate buffered solution. The buffered solution was prepared by dissolving 0.6 g sodium hydroxide and 1.6 g citric acid in 1 liter of distilled water (Cooper, 1991). The pH of the citrate buffer solution was 4.4. For initial leaching, the beakers were placed in an ultrasonic bath for 24 hours, after which they were removed and allowed to stand on the bench for three days. The leaching solution was then replaced with fresh solution (125 ml). The above procedures were repeated, after which the beakers with the blocks were then allowed to stand for a further three weeks with the leaching solution being replaced on a weekly basis. Samples of each leachate were collected and retained for copper analysis. In addition the weights of the blocks before leaching, and also at each change of leaching solution, were recorded. This allowed the correction of the leachate volume at each change of solutions to be made.

3.2.1.4 Analysis of copper and nitrogen

Analysis of copper in treated blocks

Analysis of copper in the leached copper amine treated blocks was conducted using an ASOMA™ X-ray Fluorescence Analyzer. The leached block was ground into 30

mesh sawdust for the X-ray analysis. In order to convert the X-ray data from weight percent to the more usual weight of chemical per volume of wood (kg/m^3), the wood density of each block was determined from the initial oven dried weight. The results of the copper retention were reported on an oxide (CuO) basis.

Analysis of copper in leachate of each leaching phase

The copper content in the leachate solutions was measured by an Atomic Absorption (AA) Spectrometer. Standard copper solutions (2 ppm, 4 ppm, 6 ppm, 8 ppm, 10 ppm) were prepared by serially diluting a commercial 1000 ppm standard copper solution. All the leachate solutions were diluted to provide a suitable copper concentration for the AA analysis.

The initial retention of copper in blocks prior to leaching, was calculated from the sum of the residual copper in the blocks, and the total copper determined from all of the leachates.

Analysis of nitrogen in the leached blocks

A 0.1 g aliquot of treated sawdust was placed into a Kjeldahl digestion tube. To each sample was added a half of a tablet of Kjeldahl catalyst (5.0 g K_2SO_4, 0.15 g $CuSO_4$ and 0.15 g TiO_2). The tubes were set on the digestion rack in the heating mantle, and then 5 ml of 98% conc. sulfuric acid was carefully added to each tube. After the sulfuric acid had been added, the samples were heated to about 400 ^0C and the digestion allowed to proceed for two hours. The endpoint for digestion was identified by the formation of a clear lime-green liquid which showed no effervescence. The digestion tubes were then

removed from the heating mantle and allowed to cool to room temperature prior to being diluted (Anonymous, 1981).

The nitrogen analysis was performed with the Kjeldahl technique using a Lachat QuikChem™ Automated Ion Analyzer. Each digested solution (5 ml) was diluted to ensure that the acid concentration was lower than 4 %. From a preliminary test analysis, it was found that the amine solution could not be analyzed directly to measure the nitrogen content in the leachate, using the ion analyzer. It was caused by the incomplete conversion of the nitrogen in amine and copper-amine solutions to the detectable ammonia by using the conventional Kjeldahl technique. Therefore, only the digested solids were analyzed for nitrogen.

3.2.2 Leaching experiment of copper-HDO amine treated wood

3.2.2.1. Treating solutions

The copper-HDO polyethylenimine (mixed with monoethanolamine) (CuHDO-Polyim), and copper-HDO aminoethylethanolamine (CuHDO-AEEA) solutions were supplied by Dr. Wolman GmbH. Both of those solutions contain 25% $Cu(HDO)_2$. The copper-HDO ethylenediamine (CuHDO-en) and copper-HDO diaminopropane (CuHDO-DAP) solutions were prepared in the laboratory by dissolving $Cu(HDO)_2$ (technical grade) in 9.5% (by weight) ethylenediamine and 15% (by weight) diaminopropane solutions, respectively. The resulting 5% copper-HDO solution (about 1.13% CuO) had a mole ratio of amine to copper of 2:1. In order to obtain about 1% copper concentration, the original CuHDO-Polyim and CuHDO-AEEA solutions and the prepared CuHDO-en and CuHDO-DAP solutions were diluted 5 times. Since a large excess of monoethanolamine was required to form a copper-HDO monoethanolamine (CuHDO-

MEA) solution, the stability of which is in doubt, this formulation was not studied. The actual concentrations of copper (expressed as CuO) in the copper-HDO amine solutions were determined by X-ray analysis. The mole ratio of amine to copper and the copper concentration (expressed as CuO) in the diluted solutions are shown in Table 3-3.

Table 3-3. Mole ratio of amine to copper and concentration of copper-HDO amine solutions after dilution.

CuHDO-amines	CuHDO-en	CuHDO-DAP	CuHDO-AEEA	CuHDO-Polyim
Amine:Cu	2:1	2:1	5:1	5:1
Concentration of CuO (%)	1.12	1.13	1.14	1.13

3.2.2.2. Sample treatment and leaching assessment

Scots pine (*Pinus sylvestris*) sapwood block (50 x 25 x 15 mm) was used in this study. The treating process of the blocks with copper-HDO amine solutions was the same as that with the copper amine solutions (See 3.2.1.2), and the same leaching regime of copper amine treated blocks was applied to the copper-HDO amine treated blocks.

3.2.2.3. Analysis of copper and nitrogen

Analysis of copper in treated blocks and leachate in each leaching phase

The analysis of copper in leached copper-HDO amine treated blocks was conducted by using an ASOMA™ X-ray Fluorescence Analyzer. The analysis process was the same as that used in the leached copper amine treated samples (See 3.2.1.4).

The copper content in the leachate solutions was measured by AA spectrometry. Standard copper solutions (2 ppm, 4 ppm, 6 ppm, 8 ppm, 10 ppm) were prepared by serially diluting a commercial 1000 ppm standard copper solution. The ultrasonic leachates from copper-HDO amine treated samples, contained a small amount of precipitate, which came from the surface of the blocks. This precipitate was separated by centrifuging at 3000 r/min. for 5 min. The solution was then decanted leaving the precipitate, which was dissolved by the addition of a minimum amount of ethylenediamine solution (50 % by weight). The total volume of the dissolved solution was recorded. The resulting solutions and all of the leached solutions were diluted to provide a suitable copper concentration for the AA analysis.

Determination of total copper in treated blocks

The initial retention of copper in blocks prior to leaching, was calculated from the sum of the residual copper in the blocks, and the total copper determined from all of the leachates, which also included the recovered copper precipitate formed on the surface. In selected blocks the weight uptake was recorded for unleached blocks, which were then analyzed. The data was consistent with that based on the leachate and x-ray analysis.

3.2.2.4. Analysis of nitrogen and HDO in the leached blocks

Analysis of nitrogen in the leached blocks

The methodology (digestion process and Kjeldahl measurement method) applied for analyzing nitrogen in the leached copper-HDO amine treated blocks is the same as that used for the copper-amine treatment. The nitrogen in the pure chemicals $Cu(HDO)_2$

and $KHDO.H_2O$ were also examined by using the Kjedahl technique. Only 10 % of HDO was recovered by this analysis method.

Analysis of HDO in the leached blocks

The analysis of HDO in the leached blocks was carried by Dr. Wolman GmbH using a Perkin Elmer LC Series 200 instrument. The leached blocks were ground to sawdust, and dried overnight at 80 °C. The dried wood meal was subjected to the following extraction process twice. A 0.5 g sample of the wood meal was weighed into a 100 ml Erlenmeyer flask, after which 10.0 ml methanol and 40.0 ml eluent solution (0.05 M potassium dihydrogenphosphate solution and methanol in the ratio of 55 to 45%) were added. The wood meal in the flask was then stirred vigorously for one hour at room temperature. Afterwards, the wood meal was filtered, and the filtrate collected into a 100 ml graduated flask. The wood meal was returned to the Erlenmeyer flask to repeat the extraction. The filtrates from each extraction were combined into the same 100 ml graduated flask, and filled up to the mark with the eluent solution. A representative sample of the filtrate was injected into the HPLC to measure the concentration of HDO. This analysis method can recover 80 % of the HDO in the wood samples. The instrument parameters and operating conditions are shown in Table 3-4.

Table 3-4. Instrument parameters and operating conditions.

Column	LiChrospher RP 60 select B (5µm)
Size of column	125 mm in length and 4 mm in the internal diameter
Precolumn	LiChrospher RP 60 select B (5µm), 4 x 4 mm
Flow	1.2 ml/min
Wavelength	229 nm
Eluent	55 % 0.05 M KH_2PO_4 solution 45 % Methanol p. a. After mixing, the pH of the eluent is adjusted to 2.5 with H_3PO_4.
Run time	8 min
Retention time	About 2.5 min

3.2.3. The influence of mole ratio of AEEAH to copper on the leachability

Cu-amines (Cu-MEA, Cu-en, Cu-DAP, Cu-AEEA and Cu-Polyim), CuHDO-AEEA, CuHDO-Polyim, and pure aminoethylethanolamine (AEEAH) were provided by Dr. Wolman GmbH. CuHDO-en and CuHDO-DAP were prepared in the laboratory (see Section 3.2.2). A small amount of CuHDO-MEA solution (1% Cu concentration) was also prepared by adding solid $Cu(HDO)_2$ to monoethanolamine solution with the mole ratio of MEAH to Cu of 8:1. The mole ratio of amine to copper is listed in Table 3-5. A series of Cu-AEEA and CuHDO-AEEA solutions with different mole ratios of AEEAH to Cu of 5:1, 4:1, 3:1, and 2:1 were obtained by adding AEEAH to the original Cu-AEEA solution or adding $Cu(HDO)_2$ solid to original CuHDO-AEEA solution. Since it is difficult to gain a clear and stable CuHDO-AEEA solution with the low AEEAH to Cu mole ratio of 2:1, this ratio was adjusted to 2.3 to 1. In order to measure the absorption wavelength in the UV-Vis for each solution, the Cu-amine and CuHDO-amine solutions, as well as the Cu-AEEA and CuHDO-AEEA solutions with different AEEAH to copper ratios, were then diluted with distilled water to reach a concentration of copper 0.1%. The UV-Vis spectra of these solutions were recorded with a Varian Gary 3 Spectrophotometer™ in the range of 400 to 800 nm.

CuHDO-AEEA solutions with the different AEEAH to copper mole ratio were diluted to 1% copper concentration (expressed as CuO). The Scots pine sapwood blocks (25 x 15 x 5 mm) were then treated with the prepared CuHDO-AEEA solutions. The treating process was the same as that used for copper-amine and copper-HDO amine treatments (see section 3.2.1). Six blocks were treated with each solution to supply three blocks for water leaching and three blocks for citrate buffer leaching. The leaching

Table 3-5. The mole ratio of amine to copper and the absorption maxima in UV-Vis spectra of Cu-amine and CuHDO-amine solutions.

Cu-amines			CuHDO-amines		
Sample ID	Mole ratio	Wavelength (nm)	Sample ID	Mole ratio	Wavelength (nm)
Cu-MEA	4:1	629	CuHDO-MEA	8:1	641
Cu-Polyim	2:1	642	CuHDO-Polyim	5:1	639
Cu-en	2:1	566	CuHDO-en	2:1	556
Cu-DAP	2:1	617	CuHDO-DAP	2:1	615
Cu-AEEA5	5:1	664	CuHDO-AEEA5	5:1	617
Cu-AEEA4	4:1	664	CuHDO-AEEA4	4:1	608
Cu-AEEA3	3:1	660	CuHDO-AEEA3	3:1	604
Cu-AEEA2	2:1	651	CuHDO-AEEA2	2.3:1	594

regime was slightly different from the previous design for the copper-HDO amine treatment. From the leaching test with copper-amine or copper-HDO amine treated blocks, it was determined that the first two ultrasonic leaching stages plus one phase of static leaching removed over 95 % of leachable copper (see section 3.3.1. and 3.3.2.). Therefore, the wood blocks treated with the CuHDO-AEEA solutions with the different mole ratios of AEEAH to Cu, were only subjected to two phases of ultrasonic leaching and one phase of static leaching instead of two phases of ultrasonic and three phases of static leaching.

The copper remained in the leached blocks was analyzed by an ASOMA™ X-ray Fluorescence Analyzer, while the copper contents in the leachate solutions were measured by AA. The purple precipitate in the leachates from the ultrasonic leaching was collected and dissolved by the addition of a minimum amount of AEEAH solution (50 %). The total volume of the dissolved solution was recorded, and the copper content in the solution containing the purple precipitate was measured by AA separately.

The initial retention of copper in the blocks before leaching, was determined from the sum of the residual copper in the blocks, and the total copper from all of the leachates including the recovered copper precipitates, formed during leaching.

3.3. Results and discussion

3.3.1 Leaching resistance of copper-amine treated wood

3.3.1.1. Recovery of amine during distilled water and citrate buffer leaching

Wood is slightly acidic (pH is about 4), so it was expected that during amine treatment, reaction with the more reactive carboxylic acid groups to produce amine-acid salts, will cause some of the amine to bind to the wood. The remainder will be readily leached. The residual nitrogen retained in treated blocks, after leaching with distilled water and citrate buffer leaching of amine treated wood, is shown in Table 3-6. The nitrogen remaining in the leached blocks was similar for the ethylenediamine and diaminopropane treatments, but was much higher than monoethanolamine. Since the nitrogen content in the leached blocks relates to the degree of wood-amine interaction, and taking into account the fact that ethylenediamine and diaminopropane contain twice as much nitrogen as ethanolamine, it may be concluded that the three amines reacted to a similar degree in wood. It was also interesting to note that, only a small decrease in the nitrogen content was observed after the citrate buffer leaching. This suggested that the product formed from the amine wood interaction is very stable, not only in distilled water but also in the citrate buffer solution. The amine-wood products are resistant to being dissolved or broken down by the buffer solution.

Table 3-6. The nitrogen and amine content in leached amine and copper-amine treated Scots pine blocks.

Treatment Group	N (mmg/g wood)		Amine (mmol/g wood)	
	Water	Buffer	Water	Buffer
MEAH	3.95 (0.25)*	2.90 (0.18)	0.282	0.207
en	7.27 (0.24)	6.49 (0.12)	0.260	0.232
DAP	5.85 (0.13)	5.50 (0.17)	0.209	0.196
Cu-MEA	4.19 (0.23)	3.38 (0.10)	0.299	0.241
Cu-en	4.80 (0.21)	3.87 (0.20)	0.171	0.139
Cu-DAP	6.61 (0.31)	4.61 (0.15)	0.236	0.165
Cu-AEEA	5.22 (0.20)	3.79 (0.11)	0.186	0.136
Cu-Polyim	5.83 (0.15)	4.43 (0.19)	0.416	0.316

* Standard deviation

3.3.1.2 Leaching of copper and amine from copper-amine treated wood

The copper retentions for the copper amine treated blocks were ca. 11.0 to 12.0 kg/m^3. (Figure 3-1). For copper amine treated samples, the first two phases of ultrasonic leaching removed over 85 % of the leachable copper (Figure 3-2). After completion of the leaching process, the blocks impregnated with Cu-MEA and Cu-Polyim showed the greatest leaching resistance to distilled water, with over 80% of the copper remaining (Figure 3-3, Table 3-7). Similarly, the citrate buffered leaching removed about the same amount of copper from the blocks treated with Cu-MEA as those impregnated with Cu-Polyim. The formulation of Cu-Polyim actually contains 20% by weight of monoethanolamine solvent. The similar leaching behavior suggests that the

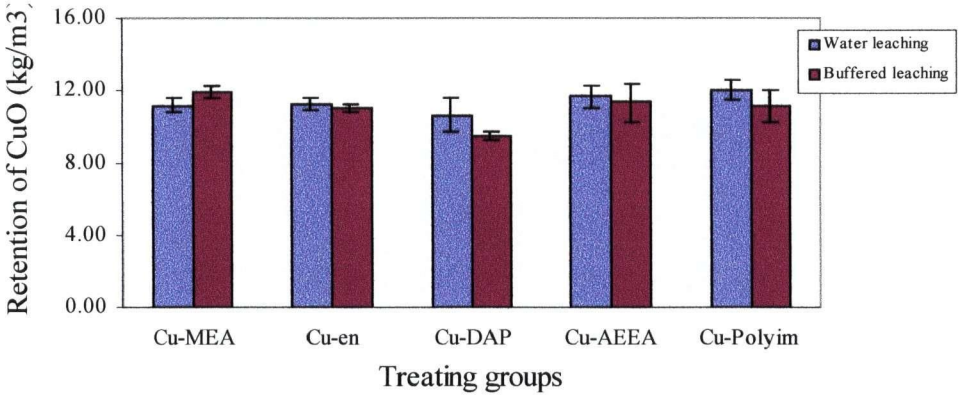


Figure 3-1. Copper retention (expressed as CuO kg/m^3) in unleached copper-amine treated Scots pine blocks.

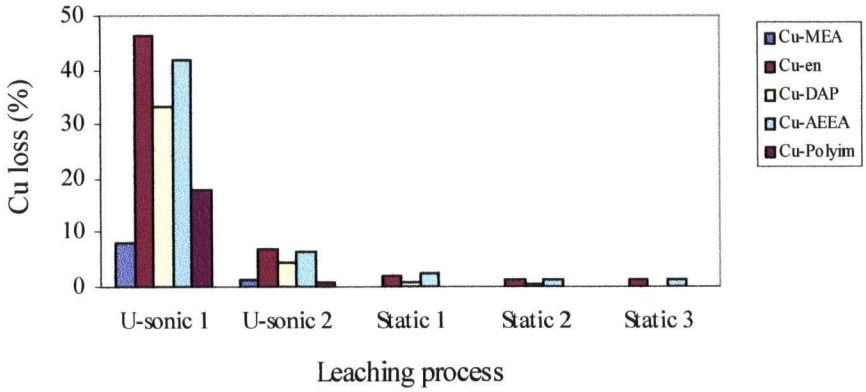


Figure 3-2. Percent copper (expressed as CuO) remaining in water leached copper-amine treated Scots pine blocks.

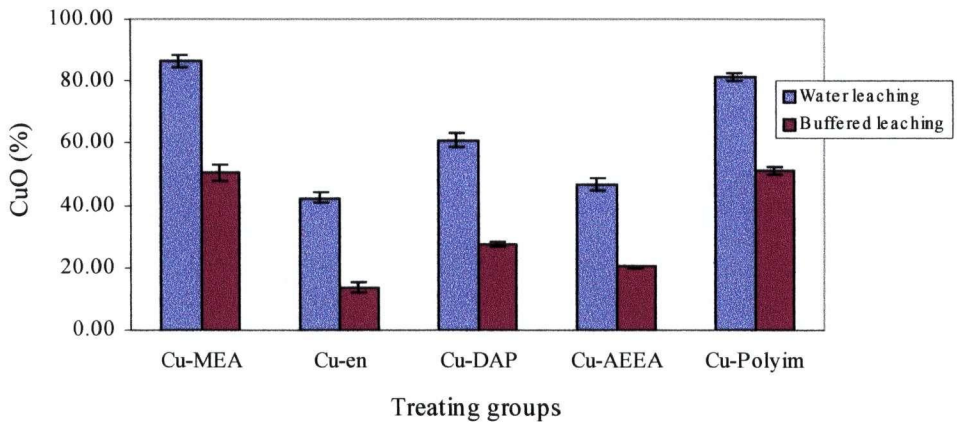


Figure 3-3. Percent copper (expressed as CuO) remaining in leached copper-amine treated Scots pine blocks.

Table 3-7. Copper content in copper-amine treated Scots pine blocks before and after the completion of leaching.

Treatment group	Leaching solution	**Initial retention of CuO (kg/m^3)	CuO remaining after leaching (%)	Cu (mmol/g)
Cu-MEA	water	11.19 (0.4)*	86.36 (1.8)	0.210
Cu-MEA	buffer	11.93 (0.3)	50.62 (2.3)	0.133
Cu-en	water	11.28 (0.3)	42.40 (1.6)	0.101
Cu-en	buffer	11.04 (0.2)	13.64 (1.7)	0.032
Cu-DAP	water	10.64 (0.9)	61.45 (2.0)	0.143
Cu-DAP	buffer	9.52 (0.2)	27.57 (0.8)	0.056
Cu-AEEA	water	11.65 (0.6)	46.71 (2.1)	0.116
Cu-AEEA	buffer	11.32 (1.0)	20.44 (0.3)	0.049
Cu-Polyim	water	12.03 (0.5)	81.22 (1.3)	0.205
Cu-Polyim	buffer	11.15 (0.9)	51.26 (1.5)	0.118

* Standard deviation

** Initial retention determined by sum of X-ray analysis of leached blocks and AA analysis of leachate

monoethanolamine is primarily responsible for the copper complexing or reacting with wood, while the polyimine acts to stabilize the Cu-MEA complex in solution.

Of the five copper-amine treatments, the Cu-en samples retained the lowest amount of copper after either water or citrate buffered leaching (Figure 3-3). This clearly demonstrates that the copper insolubilisation/fixation reaction for Cu-en and wood is much less than that between other copper amine solutions and wood. This may be attributed to the formation of a very stable [bis(ethylenediamine)copper]$^{2+}$ cation with a very polar interaction to wood components. In addition, the highly basic nature of ethylenediamine will tend to cleave acetyl groups from hemicellulose producing acetic acid, which can react with copper to produce water-soluble copper acetate (Sjostrom, 1992).

On the other hand, the copper monoethanolamine is not able to produce stable cationic species like ethylenediamine, but forms instead more covalently bonded copper-amine complexes. The maximum number of ligand molecules which can bind to the cupric metal ion is two, at both low and high ligand-to-metal ratios (Casassas, et. al., 1989). When the pH of the solution is between 7 and 10, only the hydroxyl group of one ethanolamine ligand is deprotonated [CuMEAH.MEA]$^{+1}$. As the pH value increases above 10, the copper amine complex becomes a non-ionic species [Cu(MEA)$_2$] with no residual charge (Tauler and Casassas, 1986). Increasing the monoethanolamine to copper mole ratio in solution improves the stability of the copper-monoethanolamine (Hancock, 1981), so that for solutions with an excess of ethanolamine, the [Cu(MEA)$_2$] species is stabilized. However, once in contact with the wood, this readily decomposes forming an ethanolamine-copper-wood complex, a copper-wood compound or a simple copper

precipitate (such as copper hydroxide or carbonate). Previous research has suggested that copper-wood compounds and precipitates are readily removed by citrate buffered leaching (Jiang and Ruddick, 1997). From the data in Table 3-7, 50% of the copper resisted leaching in the buffer solution, and this is considered to arise from the more insoluble ethanolamine-copper-wood complexes.

The stability of copper chelated complexes is affected by two factors, the donor atom on the ligand and the size of the ring formed during chelation. It is well established that nitrogen forms stronger donor bonds to copper than oxygen, and that five membered chelating ligands are more stable than six membered rings (Cotton and Wilkinson, 1962). Based on this, it would be expected that the Cu-DAP treatment would be more leachable than the polyimine, but less than the Cu-en treatment. This is observed to be the case (Figure 3-3, Table 3-7). It is also known that the copper, bonded to two ethylenediamine molecules $[Cu(en)_2]^{2+}$ (equilibrium constant 20.03), is much more stable than the 1:1 complex $[Cu(en)]^{2+}$ (equilibrium constant 10.72) (Cotton and Wilkinson, 1962).

The distilled water leaching of the copper from the Cu-AEEA treated samples was similar to that recorded for copper ethylenediamine (Table 3-7). AEEAH contains terminal primary amine and hydroxyl groups, with a secondary amine in the center of the ligand. Because of the stability of the five and six membered rings, chelation of the copper involving the hydroxyl group and the primary amine is unlikely. This leaves the possibilities of diamine chelation from the primary and secondary amine, or the chelation of the secondary amine and the hydroxyl group. With the known requirement of a high excess monoethanolamine to stabilize the copper-MEA complex in solution, the stability of this Cu-AEEA suggests that the diamine chelation is the major formation. In this case,

the behavior of Cu-AEEA would be similar to Cu-en rather than Cu-MEA. The leaching results are consistent with this interpretation. Further discussion about the chelating ability of AEEAH will be presented later in Section 3.3.3. The polyethyleneimine ligand clearly would be unable to form stable copper complexes in wood due to the bulky nature of the ligand. However, Cu-Polyim treated wood had the same leaching resistance as Cu-MEA, implying that in the Cu-Polyim solution, the dominant reaction with wood involves Cu-MEA.

Because the initial nitrogen content in the copper-amine treated block was not determined, it was not possible to examine the relationship between copper and amine depletion. However, the mole ratio of amine to copper in the leached blocks was determined, and the results were shown in Table 3-8. Except the Cu-Polyim treatment, all the water leached copper-amine treated samples have a very similar amine to copper ratio. The fact that the formulation of Cu-Polyim contains 20 % MEAH solvent, and polyimine performs as a stablizer to help Cu-MEA fix in wood better, would account for the relatively high mole ratio of amine to copper in Cu-Polyim treated wood.

Table 3-8. The mole ratio of amine to copper (mol/g wood) in leached copper-amine treated Scots pine blocks.

Sample ID.	Water leaching	Buffer leaching
	Amine : Cu	Amine:Cu
Cu-MEA	1.43	1.81
Cu-en	1.70	4.32
Cu-DAP	1.65	2.95
Cu-AEEA	1.61	2.77
Cu-Polyim	2.03	2.67

It has been proposed that the fixation of basic copper solutions in wood would proceed via several reactions, which could be summarized as the formation of amine-copper complexes to wood components, simple precipitation of copper compounds (eg. copper hydroxide or copper carbonate), and the formation of simple copper-wood compounds, without amine (Ruddick, 1996). In these amine-copper complexes, the amine:copper mole ratios would be either 2:1 or 1:1. In the simple copper precipitates or copper compounds formed without amine, the amine:copper ratio would of course be 0:1.

The copper remaining in the treated wood after leaching with the buffered solution ranged from 13-51% of the initial retention, and was significantly lower than that retained after distilled water leaching (41 to 86%) (Figure 3-3, Table 3-7). Previous research (Jiang and Ruddick, 1997) has suggested that the citrate buffer solution effectively removes copper precipitated in wood, so that at least some of this loss in copper after buffer leaching, must be assigned to the loss of any simple copper precipitates. During leaching with buffer solution, the amine to copper mole ratio increased about 30% for Cu-MEA and Cu-Polyim treatments, 75% for Cu-DAP and Cu-AEEA, and 150% for Cu-en treatment (Table 3-8). The dramatically enhanced mole ratio of amine to copper for copper diamine treatments arises from the very large loss of copper in buffer solution (from 0.101 to 0.032 mmol/g in the case of Cu-en treatment), but much smaller loss of amine (0.171 to 0.139 mmol/g) (Table 3-7). The relatively large depletion of copper by buffer solution implies that not only simple copper precipitates are removed, but also copper-amine wood complexes must be leached. It is suspected that copper-amine complexes with an amine to copper mole ratio of 1:1 could be decomposed by the citrate buffer solution to form stable copper citrate. The released amine can react

with wood irreversibly so that the amine-wood content increased, as does the amine to copper mole ratio.

It is interesting to find a trend of higher amine content (moles) associated with more copper present in the treated wood, when plotting the mole ratio of amine content after water leaching against the residual copper (Figure 3-4). It was found that the moles of amine *versus* copper provided a very good linear relationship with an R^2 value of 98%, implying that the fixation mechanism was similar for the different copper-amine treatments. The plot also suggested that about 0.05 mmol/g wood of amine (25%) reacted with wood irreversibly and that this was independent of the amine-copper reaction. The remainder of amine can then be considered bound to copper. The residual amine to copper ratio retained after water leaching is approximately 1.2.

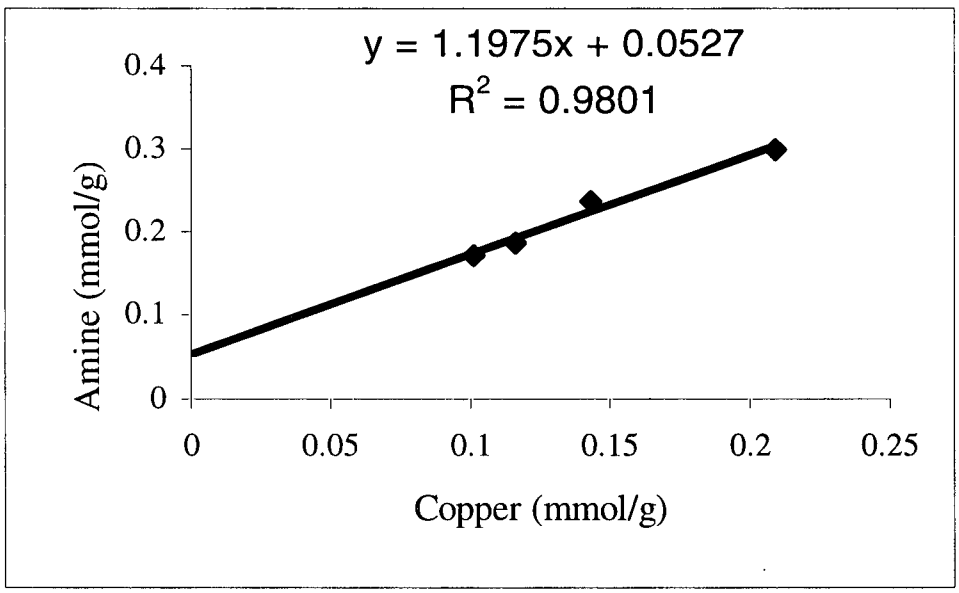


Figure 3-4. The relationship between amine and copper after water leaching.

The plot of the relationship between amine and copper after water leaching addresses the important interaction between amine and wood, and highlights that the dominant fixation products from the interaction between copper-amine solutions and wood, are copper-amine-wood complexes. However, whether they are copper(amine).wood or copper(amine)$_2$.wood complexes can not be determined from this study. If they are predominantly copper(amine)$_2$.wood complexes, however, then an almost equal amount of copper.wood compounds must be also be formed, to allow the overall ratio to approach 1.2. If copper(amine).wood complexes dominate, then, very little copper.wood compounds must be present. After buffer leaching, a linear relationship between amine and copper remains with a R^2 of 96% (Figure 3-5). However, the amount of amine reacted with wood increased to about 0.1 mmol/g wood (about 40%). It is suspected that the enhanced amine-wood reaction is caused by the release of amine during the chelation reaction between citrate buffer and copper. The released amine then reacts with wood protons to form wood.amine products that are stable in citrate buffer solution.

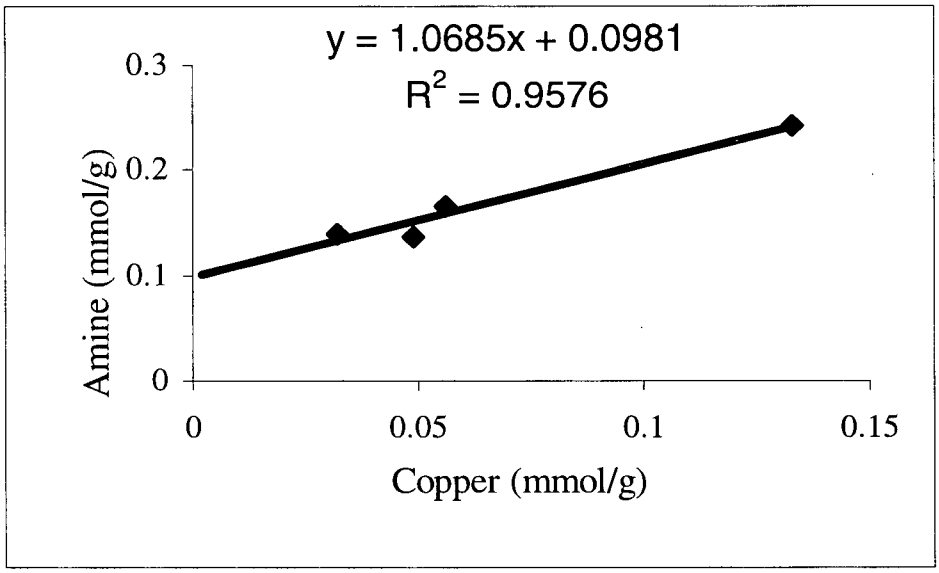


Figure 3-5. The relationship between amine and copper after buffer leaching.

3.3.2. Leaching resistance of copper-HDO amine treated wood

The initial copper retentions for the CuHDO-en, CuHDO-DAP, CuHDO-AEEA and CuHDO-Polyim were all similar (Figure 3-6). Consistent with the copper-amine leaching data, the first two stages of ultrasonic leaching removed most, (over 80%) of the unbound copper (Figure 3-7). However, the leaching resistance of the copper-amine and copper HDO-amine treated blocks were clearly different, with the HDO tending to increase the resistance of copper to leaching for CuHDO-en and CuHDO-DAP treatments (Figure 3-8). The copper retentions for CuHDO-en and CuHDO-DAP during the distilled water leaching were only reduced to 60-80% of their original values, but compared to copper-amines, the corresponding leaching resistance of CuHDO-AEEA (32%) was reduced slightly as was that of the CuHDO-Polyim (62%). The inclusion of HDO with the copper amine, enhanced the resistance of copper to depletion by the citrate buffer solution, in all cases (Table 3-9), and this change was most noticeable for the copper-HDO-diamine treatments.

The amine to copper ratio in CuHDO-AEEA is 5:1. This is much larger than that used in the Cu-AEEA treatment (2:1), and it may be hypothesized that the increased amine to copper ratio in CuHDO-AEEA stimulated chelation involving the hydroxyl group on AEEAH, so that it behaved similar to monoethanolamine. This hypothesis was supported by the similar leaching pattern of CuHDO-AEEA to that of CuHDO-Polyim (The influence of the AEEAH to copper ratio on the complexes present in solution will be discussed more fully in section 3.3.3.). The CuHDO-Polyim solution may be also

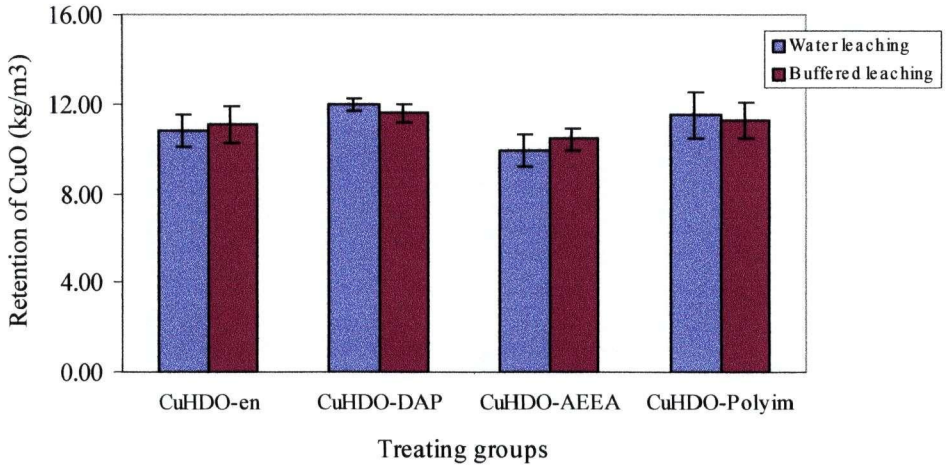


Figure 3-6. Copper retention (expressed as CuO kg/m^3) in unleached copper-HDO amine treated Scots pine blocks.

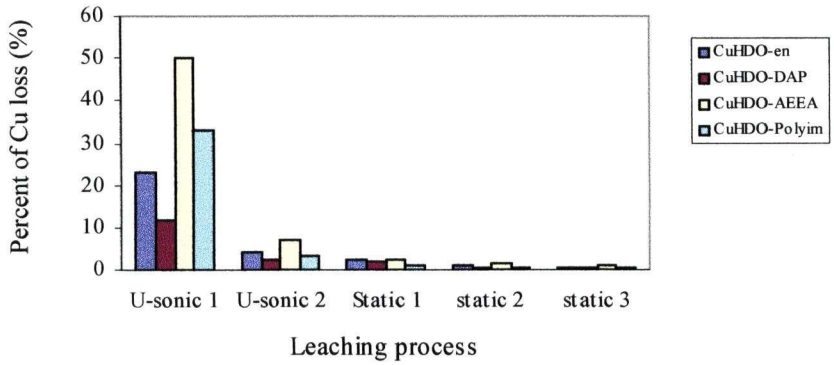


Figure 3-7. Percent copper (expressed as CuO) remaining in water leached, copper-HDO amine treated, Scots pine blocks.

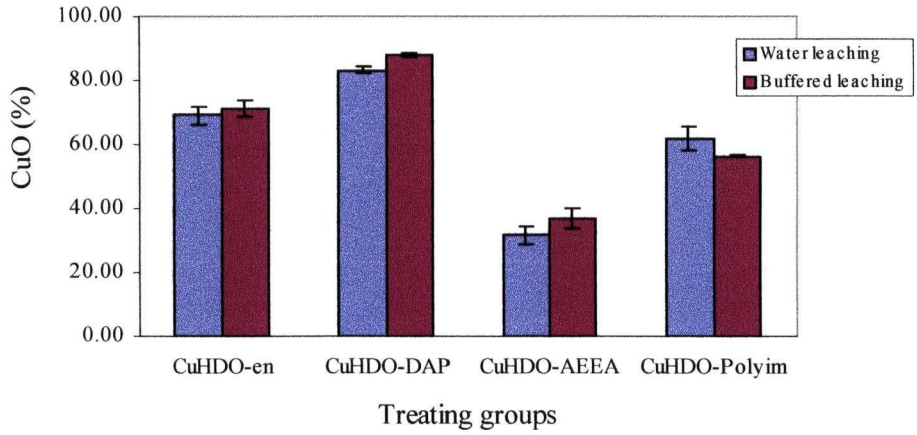


Figure 3-8. Percent copper (expressed as CuO) remaining in leached copper-HDO amine treated Scots pine blocks.

Table 3-9. Copper content in copper-HDO amine treated Scots pine blocks before and after the completion of leaching.

Treatment group	Leaching solution	Retention**of CuO (kg/m^3)	Percent remaining after leaching (%)
CuHDO-en	Water	10.82 (0.7)	69.14 (3.0)
CuHDO-en	Buffer	11.10 (0.8)	71.07 (2.6)
CuHDO-DAP	Water	11.98 (0.3)	83.27 (1.0)
CuHDO-DAP	Buffer	11.60 (0.4)	88.05 (0.7)
CuHDO-AEEA	Water	9.90 (0.7)	31.60 (3.0)
CuHDO-AEEA	Buffer	10.43 (0.5)	36.86 (3.1)
CuHDO-Polyim	Water	11.49 (1.0)	61.80 (3.8)
CuHDO-Polyim	Buffer	11.29 (0.8)	56.56 (0.6)

* Standard deviation

** Retention determined by sum of X-ray analysis of leached blocks and AA analysis of leachate

considered as a monoethanolamine system, although the large excess of the Polyim may stabilized some of the copper in solution.

The different leaching behaviors of the CuHDO-amine treatments may be influenced in terms of the relative stability of the very stable $Cu(HDO)_2$ precipitate, and that of the diamine-copper-wood complexes, both of which are resistant to leaching by the buffered citrate solution. For the two diamine-copper-HDO treatments, the reaction with wood may be considered to produce mainly $Cu(HDO)_2$, with some copper.amine.wood products also being formed. Since CuHDO-AEEA is considered to function as a monoethanolamine system, for the CuHDO-AEEA and CuHDO-Polyim treated blocks, the $Cu(HDO)_2$ is also formed to a more limited extent. In CuHDO-AEEA, copper is chelated with the hydroxyl group on AEEAH, producing competition with bonding to HDO or wood. A similar argument may be advanced for the reduction in the resistance of CuHDO-polyim treated wood. In addition, the bulky nature of the AEEAH and polyimine solvent molecules would further inhibit any tendency to form CuHDO-amine wood complexes.

Two basic reaction schemes can then be considered. One of which relates to the copper-ethylenediamine wood fixation, while the second focuses on the copper-ethanolamine wood fixation chemistry. Looking first at the copper-amine wood reactions, for ethylenediamine, some amine combines with wood protons to produce an amine acid salt (reaction #1). In addition, diaminecopper cations present in solution will react with the wood to form stable diamine.copper.wood complexes (reaction #2). However, the reactions of amine with wood will also result in lowering of the diamine-copper concentration in the reacting solution as shown in reaction #3, (and reaction #2 is

impeded). This will produce free copper ions in solution that will react with wood forming copper.wood products of low leaching resistance. The stability constant for $[Cu(en)]^{2+}$ confirms the lower stability of this form relative to either $[Cu(en)_2]^{2+}$ or Cu^{2+}.

1. $en + wood\text{-}H \rightleftharpoons en\text{-}H^+ + wood^-$

2. $[Cu(en)_2]^{2+} + 2wood^- \rightleftharpoons Cu(en)_2(wood)_2$

3. $[Cu(en)_2]^{2+} \rightarrow [Cu(en)]^{2+} + en \rightarrow Cu^{2+} + 2en$
   reacts with wood

4. $Cu^{2+} + 2HDO^- \rightarrow Cu(HDO)_2$

5. $[Cu(MEA)_2] \rightleftharpoons [Cu(MEAH).MEA]^+ \rightleftharpoons [Cu(MEAH)_2]^{2+}$
   pH > 9 pH 7-10 pH 5-8

6. $[Cu(MEA)_2] + H.wood \rightleftharpoons [CuMEAH.MEA].wood$
   stable in pH 7-10

When HDO is included in the copper-en solution, copper ions produced in reaction #3 react to form $Cu(HDO)_2$ which is very insoluble and has excellent leaching resistance (reaction #4). The formation of $Cu(HDO)_2$ precipitate, will therefore promote reaction #3 preferentially, and reaction #1 and #4 will be dominant, with reaction #2 being minor. For copper-ethanolamine.wood reactions, the ligand can be present in protonated or deprotonated forms (reaction #5). During reactions with wood, the copper-amine can absorb the proton into the complex, as shown in reaction #6. This does not lead to changes in the amine concentration so the reaction is promoted and stable copper.$(amine)_2$.wood is readily formed. It will not be a perfect reaction, since the excess amine can react with wood (similar to that shown in reaction #1 for the en), and this will complete with the formation of the copper.(amine).wood complex. The abundant reaction sites in wood and the excess amine, however, suggest that this impact will be small. When HDO is added to the system, the ready formation of $Cu(HDO)_2$ observed suggests

that its stability is greater than that of the copper.amine.wood complex, and it is formed preferentially. However, the release of the amine will promote even higher solution pH's so that the deprotonated form [$Cu(MEA)_2$] will be present. This will show a reduced tendency to react with wood, and the copper amine reaction will be negatively impacted. So for the ethanolamine type copper formulation, the formation of leach resistant $Cu(HDO)_2$ will not be as efficient as with the copper diamine system, since the reactions producing copper.amine.wood and $Cu(HDO)_2$ will compete with each other, and [Cu(MEA)] will remain in the wood.

The depletion anticipated during buffer leaching should be markedly reduced, due to the more stable $Cu(HDO)_2$ compounds. This is indeed observed (Table 3-9). Thus it may be concluded, that for CuHDO-amine, the leach resistance will depend upon the formation of a number of copper compounds which included: $Cu(HDO)_2$, Cu-amine-wood, Cu-wood, and copper acetate. The first two are considered to be stable and leach resistant, but the leach resistance of the others will be lower.

The results from the HDO analysis of leached copper-HDO amine treated blocks are shown in Table 3-10 (corrected for the 80% recovery). The blocks treated with the copper-diamine systems, CuHDO-en and CuHDO-DAP, contained the highest HDO after water and buffer leaching. On the other hand, CuHDO-AEEA had the lowest HDO retention after leaching. Since $Cu(HDO)_2$ is known to be a very stable precipitate even in citrate buffered solutions, the higher HDO retention is almost certainly associated with the greater ability to form $Cu(HDO)_2$ precipitate. The HDO remaining in the leached blocks is in agreement with the leaching behavior of the copper in the CuHDO-amine

Table 3-10. Results of nitrogen and HDO analysis in the leached blocks treated with copper-HDO amine solutions.

Sample ID	Water leaching				Buffer leaching			
	N* (mg/g)	HDO (mg/g)	$Cu_{leftover}$ (mg/g)	Amine: $Cu_{leftover}$	N* (mg/g)	HDO (mg/g)	$Cu_{leftover}$ (mg/g)	Amine: $Cu_{leftover}$
CuHDO -en	4.02	33.23	3.11	2.93	3.11	36.96	2.74	2.57
CuHDO -DAP	3.13	42.12	3.94	1.80	2.52	44.70	4.11	1.39
CuHDO -AEEA	4.91	9.68	2.70	4.12	4.55	18.46	2.06	5.15
CuHDO -Polyim	8.48	13.71	5.63	6.88	8.87	17.93	3.65	10.98

* Nitrogen from amine

treatments. The enhanced HDO content in the leached blocks is related to the increased leaching resistance of the copper.

According to the proposed reaction scheme, for diamine copper-HDO systems (CuHDO-en and CuHDO-DAP), the most dominant product after fixation is $Cu(HDO)_2$ which requires two moles of HDO and one mole of copper. However, for CuHDO-AEEA and CuHDO-Polyim treatments (AEEAH is considered as an ethanolamine type ligand at the high concentrations of amine in CuHDO-AEEA solution), both $Cu(HDO)_2$ and [Cu(MEAH)(MEA).wood] are present in the wood and are leach resistant. This will impair the formation of $Cu(HDO)_2$, resulting in a lower leaching resistance for CuHDO-AEEA. Similarly, the CuHDO-Polyim shows lower leach resistance than the corresponding copper-HDO diamine treatments, but higher than the CuHDO-AEEA. Presumably the excess polyimine is able to promote the formation of $Cu(HDO)_2$. The amount of copper complexes containing no HDO in the leached wood samples, was calculated and listed in Table 3-10. About 70% of the copper formed the $Cu(HDO)_2$ for

CuHDO-en and CuHDO-DAP treatments, for both water and buffer leaching. For CuHDO-AEEA and CuHDO-Polyim treatments, the amount of $Cu(HDO)_2$ is much less, being 44% and 36%, respectively. After the formation of $Cu(HDO)_2$, the remaining copper and amine are free to react with the wood, during which the fixation reaction is as described earlier for copper-amine treated wood.

After citrate buffer leaching, the copper remaining in the CuHDO-amine treated samples appeared to increase slightly in these three cases (Table 3-9). However, the differences were not significant.

Since the Kjeldahl method could only detect about 10% of the anticipated nitrogen from HDO during the digestion and titration, the nitrogen analyzed is considered to mainly be derived from the amine. The amount of amine nitrogen was determined by deducting 10% nitrogen allocated to HDO in the copper-HDO amine treated samples. Based on the amine nitrogen data and the residual copper left after accounting for that in $Cu(HDO)_2$, the amine to residual copper mole ratio was calculated and is shown in Table 3-10. Considering only the residual copper, all CuHDO-amine treated blocks exhibited an increased amine to copper ratio compared to that for the corresponding Cu-amine treatments. This is to be expected, since a significant amount of the copper has been removed during formation of $Cu(HDO)_2$, so that the ratio of amine to copper left in the solution will be very high, enhancing the formation of copper-amine-wood complexes. This should have increased the leaching resistance, but this was not the case when ethanolamine solvents were present. This may be due to the formation of stable, but soluble copper.HDO.amine complexes. Alternatively, the higher amine content may also increase the acetyl cleavage, leading to more water-soluble copper acetate being formed.

3.3.3. The influence of mole ratio of AEEAH to copper on the leachability

AEEAH has a primary amine and a hydroxyl group on either end of the molecule, with a secondary amine in the center of the ligand (Figure 3-9 a). Because of the greater stability of the five and six membered rings compared to seven or greater ring systems, chelation involving the hydroxyl group and the primary amine is unlikely. This leaves the possibilities of diamine chelation from the primary and secondary amine, or the chelation of the secondary amine and the hydroxyl group (Figure 3-9 b and c). These two types of chelation imply the potential functions of AEEAH as diamine or monoethanolamine.

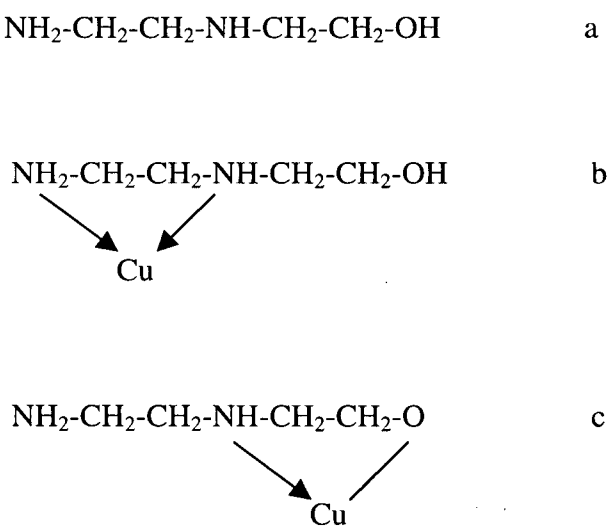


Figure 3-9. Molecular structure of AEEAH (a), and two possible options for copper chelation (b and c).

The absorption maxima in Cu-AEEA and CuHDO-AEEA solutions with the different mole ratios of AEEAH to Cu from the UV-Vis measurement was listed in Table 3-5. It was found for both Cu-AEEA and CuHDO-AEEA solution, that increasing the mole ratio of AEEAH to Cu, the maximum moved to higher wavelength, approaching the position of the maximum wavelength of the copper-monoethanolamine system. Lowering the mole ratio of AEEAH to Cu, led to a shift of the maximum to lower wavelength, more similar to that for a copper-diamine system. The mole ratio of AEEAH to Cu used in the Cu-amine leaching experiment was 2:1, the same as that in Cu-en solution. In this case, the leaching behavior of Cu-AEEA would be similar to Cu-en rather than Cu-MEA. The leaching results are consistent with this proposal that the diamine chelation is the major formation in the Cu-AEEA solution under the low mole ratio of AEEAH to copper.

On the other hand, in copper-HDO amine leaching experiment, the mole ratio of AEEAH to Cu was 5:1, which was the same ratio used in CuHDO-Polyim solution. With the high mole ratio of AEEAH to Cu, CuHDO-AEEA solution is expected to behave more like a copper-HDO monoethanolamine system. The formulation CuHDO-Polyim contained 20% (by weight) of monoethanolamine, which is primarily responsible for the copper complexing or reacting with wood. The polyimine acts as a stabilizer in the CuHDO-Polyim solution. Therefore, the leaching behavior of CuHDO-AEEA treated wood with the high AEEAH to Cu ratio should be similar to that of CuHDO-Polyim treatment. The leaching results from copper-HDO amine treated blocks again are in good agreement with this proposal, confirming the monoethanolamine chelation in CuHDO-AEEA solution becomes the dominant formation when the mole ratio of AEEAH to Cu is high.

The leachability of the wood blocks treated with CuHDO-AEEEA with the different AEEAH to copper ratios was examined, and the results are shown in Figure 3-10. Lowering the mole ratio of AEEAH to Cu in CuHDO-AEEA solutions caused the leaching resistance of copper to increase against both water and citrate buffer leaching. When the mole ratio of AEEAH to Cu was 5:1 in CuHDO-AEEA solution, the CuHDO-AEEA treated blocks only contained about 40% of the copper after leaching. This may be interpreted in terms of the relative stability of copper-HDO-ethanolamine complexes, which may be leachable. However, it is not possible to exclude the influence of the higher AEEAH content on acetyl cleavage, leading to more water soluble copper acetate

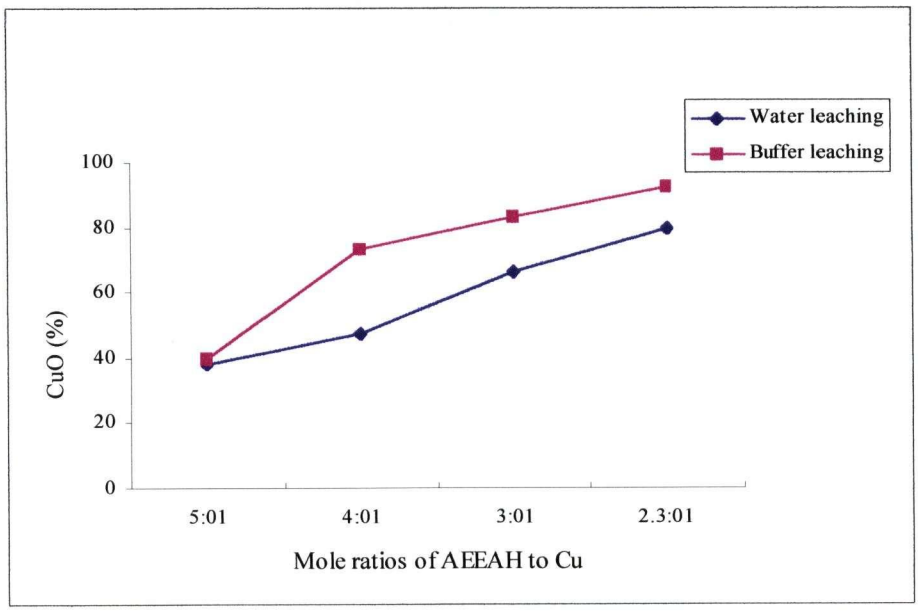


Figure 3-10. CuO remaining of CuHDO-AEEA treated blocks after leaching.

being formed. When the mole ratio of AEEAH to Cu decreased to 2.3:1, over 80% of the copper was retained in the leached blocks. The mole ratio of AEEAH to Cu (2.3:1) in CuHDO-AEEA is similar to that of CuHDO-en (2:1) or CuHDO-DAP (2:1), resulting in the leaching performance of this CuHDO-AEEA solution being similar to those of the copper-HDO diamine treatments, CuHDO-en and CuHDO-DAP. This confirms that the CuHDO-AEEA solution functions more like a copper-HDO-diamine system with the low mole ratio of AEEAH to Cu 2.3:1. This conclusion is also supported by the observation from the UV-Vis measurement (see Section 3.2.3. Table 3-5).

For all the mole ratios, the citrate buffer solution appeared to enhance the leaching resistance. It is suggested that the formation of $Cu(HDO)_2$ precipitate (at low mole ratios of AEEAH to Cu) or copper-AEEA-HDO complex (at high mole ratios of AEEAH to Cu) is improved under the slightly acidic condition. Other evidence to support this interpretation could be found in the leaching of CuHDO-en and CuHDO-DAP treated wood blocks with citrate buffer solutions (see Section 3.3.2). A slightly higher amount of copper remained for both treatments after citrate buffer leaching compared to water leaching.

3.4. Conclusions

1. Of the five copper amine treatments, wood impregnated with Cu-MEA and Cu-Polyim had the highest leaching resistance to distilled water or citrate buffer leaching. Cu-diamine treatments (Cu-en, Cu-DAP and Cu-AEEA) showed lower leaching resistance.
2. In copper amine treated wood, citrate buffer leaching removed significantly more copper and amine than distilled water.
3. In amine treated wood, the reaction between amine and wood resulted in the formation of stable products, which resisted to both distilled water leaching and citrate buffer leaching.
4. Based on the leaching study of copper-amine treated wood alone, it is not possible to confirm the dominant copper amine species formed in the wood after fixation.
5. Copper-HDO amine treated wood exhibited similar leach resistance to both distilled water and citrate buffer. CuHDO-AEEA treated wood leached copper more readily than the other three formulations.
6. Copper HDO-diamine treatments resisted leaching to the greatest extent with more than 70 % of the copper remaining following citrate buffer leaching.
7. $Cu(HDO)_2$ precipitate is formed in copper-HDO amine treated wood during leaching. Up to 70% of the $Cu(HDO)_2$ precipitate is formed in CuHDO-en and CuHDO-DAP treated wood samples. For CuHDO-AEEA and CuHDO-Polyim treatments, it is suggested that the presence of stable copper-amine-HDO complexes in solution reduces the formation of $Cu(HDO)_2$ during reaction with wood.

8. With the high mole ratio of AEEAH to Cu, the amine behaved as an ethanolamine system, while AEEAH at low mole ratio, it functioned as a diamine system.
9. In CuHDO-AEEA treatment, decreasing the mole ratio of AEEAH to Cu enhanced the leaching resistance. The leachability of CuHDO-AEEA (2.3:1) was similar to that of copper-HDO diamine treatments.
10. The leaching resistance of copper is improved during citrate buffer leaching. It is suggested that the citrate buffer solution enhances $Cu(HDO)_2$ by decomposing the copper-amine-HDO complex.

Chapter 4

Fixation reactions of wood with copper-amine and copper-HDO amine solutions

4.1. Introduction

The fixation of ammoniacal copper preservatives is initiated by the rapid loss of ammonia which causes the tetra-aminecopper complex present in the treating solution to break down. The products formed during the fixation reaction are known to include diammine-copper(II) compounds, formed either with co-biocides and/or with reactive sites on wood components, such as lignin, extractives and hemicellulose (Ruddick, 1996). There is little evidence to suggest that copper-cellulose compounds are formed (Lebow and Morrell, 1995; Kamdem and Zhang, 2000; Zhang and Kamdem, 2000). Recently, interest has grown in the use of amine-copper preservatives. The fixation chemistry of these preservatives differs from the corresponding ammonia based formulations, in that the reaction is initiated by the neutralization of the amine by labile protons present in wood. Such reactions would be anticipated for carboxylic acid functional groups present in hemicellulose and pectin, as well as phenolic groups and ferulic acid found in lignin (Craciun and Kamdem, 1997; Kamdem and Zhang, 2000; Ruddick, 1996; Thomason and Pasek, 1997; Zhang and Kamdem, 2000).

Several analytical techniques have been employed which can provide a valuable insight into the reactions taking place in wood during fixation. Three of these, FTIR, ESR and XPS, have proved to be particularly useful in studies of the fixation of copper or amine in wood *in-situ* (Craciun et. al., 1997; Craciun and Kamdem, 1997; Dagarin et. al., 1996; Hughes et. al., 1994; Humar and Petric, 2000; Kaldas and Cooper, 1998; Kamdem

and Zhang, 2000; Ostmeyer et. al., 1988; Pohleven et. al., 1994; Ruddick et. al., 1993; Yamamoto and Ruddick, 1993; Zhang and Kamdem, 2000). However, care is needed when interpreting the XPS data since it is a surface analysis technique. Consequently, it is very sensitive to surface contamination, as well as the formation of precipitate on the surface of the wood during treatment, or the migration of chemicals to the wood surface during sample wetting or drying, since they will influence the resulting spectra.

From the leaching study it was concluded that diaminecopper species are almost certainly present in wood, together with copper that has reacted with wood to form stable products. It is also possible that monoamine-copper-wood complexes are formed and these can not be eliminated. In order to gain further evidence which copper species are present in wood after fixation, a spectroscopic investigation of copper amine and copper-HDO amine treated wood was conducted.

The objective of this study was to investigate the interaction between southern pine (*Pinus sp.*) sapwood and selected amine, copper amine, and copper-HDO amine, solutions, using FTIR, ESR and XPS. It is expected that the FTIR spectra will allow observations of reactions of the carboxylic acid functional groups. Changes in the C(1s), N(1s) and Cu(2p) XPS spectra will confirm the formation of amine-copper(II) compounds during fixation. ESR spectra can provide further information about whether $Cu(HDO)_2$ is formed in copper-HDO amine treated wood, and whether nitrogen is present, and if so, how nitrogen is coordinated to copper in the copper-amine wood complexes formed during fixation.

4.2. Materials and methods

4.2.1. Sample preparation:

Southern pine (*Pinus* sp.) sapwood was used in this study. Due to the low-signal-to noise ratio in the FTIR spectra of thin latewood sections, only earlywood sections were selected. Tangential thin sections, 60 μm in thickness and 25 x 15 mm in area, were serially microtomed from wood blocks.

Previous studies have highlighted the influence on XPS spectra of the migration of mobile extractives to the wood surface during treatment and drying of test samples (Ruddick *et. al.,* 1993; Yamamoto and Ruddick, 1993). To remove the influence of the extractives, the sections were pre-soaked in dichloromethane for 6 hours, followed by immersion in distilled water for 1 hour, after which the surface was rinsed with small amount of distilled water. The soaking and washing of the thin sections in distilled water was repeated 4 times, to ensure complete removal of the dichloromethane solvent and any water-soluble extractives.

Three amines were used in the investigation, monoethanolamine (MEAH), ethylenediamine (en), and 1,3 diaminopropane (DAP). They were prepared as a 20% (w/w) concentration, by diluting analytical grade amines with distilled water. Copper amine solutions and copper-HDO amine solutions were either provided by Dr. Wolman GmbH, or prepared by the author in the laboratory (Section 3.2). To enhance the copper concentration, the solutions were slowly evaporated at room temperature. The obtained copper concentration is given in Table 4-1. Since a large excess of monoethanolamine (MEAH) was required to form a copper-HDO.monoethanolamine (CuHDO-MEA) solution, the pH was adjusted by addition of 10% suphuric acid. The pH of the solution

was measured with an Ascent™ pH/mV meter. The copper concentration (expressed as CuO) in the prepared CuHDO-MEA solution was very low (0.7%). The actual copper concentration (expressed in CuO) in these copper solutions was determined by x-ray fluorescence analysis. The measured pH and copper concentrations are shown in Table 4-1.

Table 4-1. The concentration of CuO in copper-amine solutions.

Sample ID	CuO concentration (%)	pH
Cu-MEA	6.7	11.16
Cu-en	6.6	10.86
Cu-DAP	4.1	10.12
Cu-AEEA	7.0	10.54
Cu-Polyim	6.7	11.43
CuHDO-MEA	0.7	11.00
CuHDO-en	3.3	12.05
CuHDO-DAP	3.7	12.30
CuHDO-AEEA	4.2	11.43
CuHDO-Polyim	4.6	11.57

The extractive-free sections were air dried overnight, before being soaked in either amine solution or copper-amine solution for 2 hours. Four matching sections provided replicates for each treatment, two of which were subjected to leaching. After treatment, the thin sections were stored at ambient temperature for ten days to allow completion of any chemical fixation reactions. The samples to be leached were soaked in distilled water for a total of three hours, with the distilled water being replaced every

hour. The leached sections were then air-dried for two days, and stored in desiccators containing anhydrous calcium sulphate to complete their drying.

Pure crystalline diaminoethane.copper(II) nitrate [$Cu(en)_2(NO_3)_2$] was prepared as follows: copper nitrate (0.05 mol) was dissolved in a minimum of warm distilled water (50°C), and to this was slowly added ethylenediamine (0.1 mol). The bright blue-violet crystals formed when the solution was cooled to room temperature, were collected by filtration. The crystals were washed with a minimum of ethylenediamine, air-dried and then stored in a sealed tube for later use. The preparation of di(ammine)bis-(vanillinato)copper(II) and bis(ethanolamine.vanillinato.copper(II)) have been described previously by Xie et. al. (1995) and Ruddick et. al., (2000) respectively.

4.2.2. Spectroscopic analysis:

4.2.2.1. Fourier transformed infrared spectroscopy (FTIR)

Untreated, extracted and unextracted, earlywood sections (60μm), as well as extracted thin sections treated with amine, copper-amine, or copper-HDO-amine solutions, were examined directly by FTIR. Wood sections treated with $KHDO.H_2O$ provided a reference FTIR spectrum for the copper-HDO-amine treated samples. A Mattson 5000 ™ FTIR spectrometer with a micro-sample holder was employed for the infrared analysis. The spectra were obtained with 64 scans, at a resolution of 4 cm^{-1}, over the wavenumber range 400-4000 cm^{-1}.

4.2.2.2. UV-Visible spectroscopy

The UV-visible spectra of the copper-amine and corresponding copper-HDO amine solutions were recorded with a Varian Cary3 ™ spectrophotometer in the range 400-800 nm. Each solution was diluted with distilled water to ensure a final copper concentration of 0.1%.

4.2.2.3. X-ray photoelectron spectroscopy (XPS)

The thin sections were used directly for XPS analysis. For the pure chemicals, crystalline $[Cu(en)_2](NO_3)_2]$, di(ammine)bis(vanillinato)copper(II), and bis(ethanolamine. vanillinato.copper(II)), as well as technical grade $Cu(HDO)_2$ and analytical grade $KHDO.H_2O$, compressed pellets were prepared. A Leybold Max200™ spectrometer provided the XPS analysis, and was operated at a pressure of 1×10^{-9} mbar. The unmono-chromatized AlK_α excitation source was run at 10 kV and 20 mA. The photoelectrons emitted were collected from an area 2 mm x 4 mm. High-resolution narrow-scan spectra were measured for the C1s, O1s, N1s and Cu2p core level at the pass energy of 48 eV. Peak assignment was based upon published tables of the core level binding energies for atoms of interest. Peak areas, determined after background subtraction, were used to measure relative elemental concentrations.

Curve-fitting of XPS spectra was done using the XPSPEAK™ software program, and the spectra edited by PSI-Plot™. Since nitrogen has a similar electronegativity to oxygen, C-N bonding present in pure amine and copper amine treated samples was assigned to C2 type carbon analogous to the earlier work of Dorris and Gray (1978). The binding energy of C1 was referenced to 285.0 eV, and all other peaks were calibrated

with respect to the position of this peak. During curve-fitting, a reduction in Σ was regarded as an indicator of the relative goodness of fit, when fitting more than one peak to the spectral envelope.

4.2.2.4. Influence of X-ray analysis on sample degradation

Previous research has shown that during XPS, reduction of certain elements by the X-ray beam can occur. In order to investigate whether the spectra of N1s and Cu2p in copper amine complexes are stable during XPS analysis, crystalline $[Cu(en)_2](NO_3)_2]$ compressed into a pellet and a Cu-en treated wood section were both exposed to the X-ray irradiation for one or two hours and the acquired spectra were compared with those originally recorded.

4.2.2.5. Electron spin resonance spectroscopy (ESR)

$Cu(HDO)_2$ DMSO solution, and the copper-amine and copper-HDO amine treated Scots pine blocks from the leaching experiment (Chapter 3) were used for the ESR measurements. The distilled water and buffer leached Scots pine blocks were reduced to sawdust, and then added into the ESR quarz tube until it was filled to a height of about 4 mm. A Brucker ECS 106 ™ ESR spectrometer was used to record the spectra. Wood sawdust samples were examined at room temperature. $Cu(HDO)_2$ DMSO solution, prepared as the copper concentration of 0.01 mol/m^3, was measured at the low temperature of 150 k. The operating parameters for the ESR are shown in Table 4-2.

Table 4-2: The operating parameters for the ESR spectrometer.

General	Detection temperature	294 K/(150K for $Cu(HDO)_2$)
	Number of scans	10
Receiver	Modulation frequency	50 kHz
	Modulation amplitude	1.018 G
	Receiver gain	2.00e + 04
Signal channel	Conversion	5.12 ms
	Time constant	1.28 ms
	Sweep time	83.886 s
Field	Center field	3100.00 G
	Sweep width	1000.00 G
	Resolution	1024 points
Microwave	Power	10 mw
	Frequency	9.57 GHz

4.3. Results and discussion

4.3.1. FTIR Spectral analysis

The infrared spectra of thin sapwood sections allowed changes in the functional groups to be identified. For the extracted sample, the FTIR spectrum showed no discernable change from that of the unextracted section (Figure 4-1). This is expected, since the extractive content is low and also the functionality of the components removed is similar to the remaining structural components of wood.

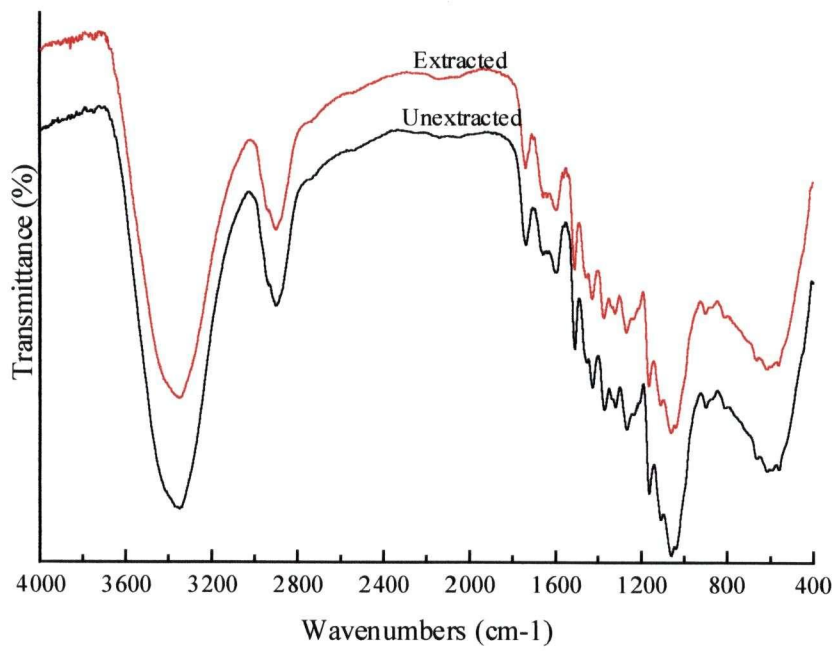


Figure 4-1: FTIR spectra of unextracted, and extracted, southern pine thin sections.

4.3.1.1. Amine treated sections

An obvious and important change in the FTIR spectra of the amine treated sections from the reference spectra of the extracted sections, was the elimination of the peak at 1735 cm^{-1} (Figures 4-2 and 4-3). This peak at 1735 cm^{-1} has been assigned to the carboxylic acid stretching vibration (Craciun et. al., 1997; Craciun and Kamdem, 1997; Hergert, 1971, Hortling et. al. 1997; Liu et. al., 1994; Tolvaj and Faix, 1995; Zhang and Kamdem, 2000). It is proposed that treatment of the thin sections with amine solutions resulted in the formation of amine-acid salts which caused the absorption at 1735 cm^{-1} to shift to 1654-1594 cm^{-1} (Figures 4-2 and 4-3). This is consistent with the assignment for the carboxylate anion by several authors (Craciun et. al., 1997; Craciun and Kamdem, 1997; Nakamoto, 1997; Williams and Fleming, 1966; and Zhang and Kamdem, 2000). N-H banding in primary amine also occurs in the range of 1654-1594 cm^{-1} (Morrison and Boyd, 1973; Nakamoto, 1997). The band at 1718 cm^{-1}, from vanillic and other conjugated esters on lignin (Sarkanen et. al. 1967a), was not observed after treatment, suggesting alkaline hydrolysis removed conjugated esters that are monofunctionally connected with lignin.

Following leaching with either distilled water or citrate buffer, the absorptions in the region 1700 to 1760 cm^{-1} did not return (Figure 4-3). This confirmed that the amine acid salts were clearly stable to hydrolysis, since leaching did not recover the free acid functionality. These findings were consistent with field observations reported previously by Ruddick (1979 and 1996) who showed that wood treated with ammoniacal copper preservatives retained enhanced nitrogen levels, even after several years of exposure.

They were also supported by the FTIR spectra of amine and naphthenic acid solutions reported by Craciun and Kamdem (1997).

The formation of an amine-carboxylic acid salt should produce an N-H bending vibration for $R\text{-}NH_3^+$ at ca.1555 cm^{-1} (Nakamoto, 1997). It was not possible to detect this peak in the unleached amine treated sections, because other bands at ca. 1570 cm^{-1} mask this wavelength.

The absorption at 1371 cm^{-1} corresponding to the ring stretching with phenolic O-H bending character (Sarkanen et. al. 1967b) also slightly decreased in the leached treated sections, compared to the untreated controls (Figure 4-3). This was caused by the interaction between amines and the phenolic hydroxyl groups in lignin, which were activated under the highly basic conditions. The absorption peak at ca.1230 cm^{-1}, assigned to the acetyl ether linkage (Sarkanen et. al. 1967a), was markedly reduced following amine treatment, a change that was not restored after water leaching. This observation suggests that cleavage of the acetyl ether linkage with the amine occurs due to alkaline hydrolysis.

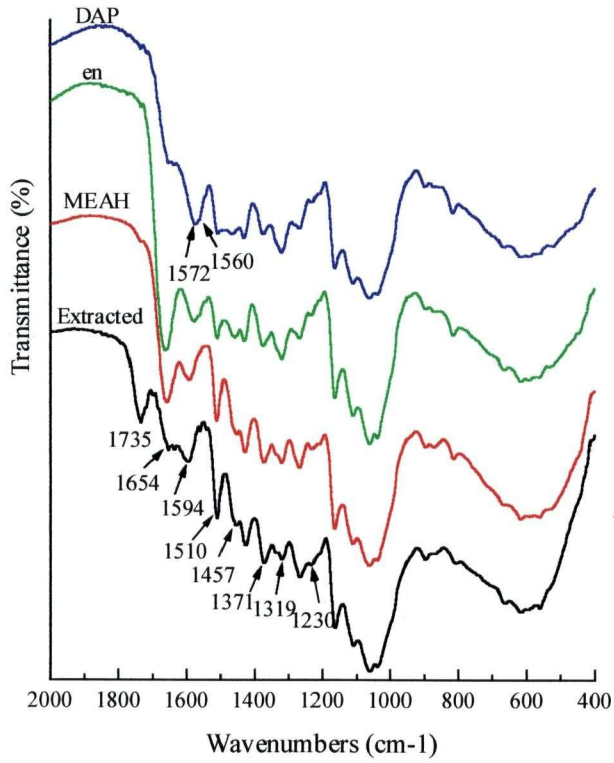


Figure 4-2. FTIR spectra of amine treated southern pine thin sections before distilled water leaching.

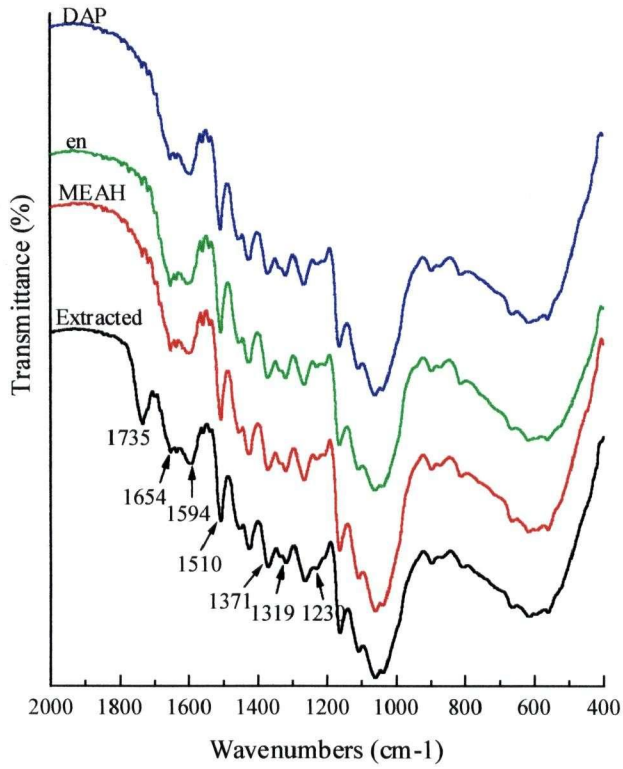


Figure 4-3. FTIR spectra of amine treated southern pine thin sections after distilled water leaching.

4.3.1.2. Copper-amine treated sections

The FTIR spectra of the copper-amine, and amine treated sections had several common features. In particular the carbonyl band at 1735 cm^{-1} in untreated wood was removed, being shifted to 1654-1594 cm^{-1}. Similarly, the absorption at 1370 cm^{-1} and 1230 cm^{-1} which were reduced in the amine treated sections was also reduced by the copper-amine treatment. In all of the FTIR spectra of unleached and leached copper-amine treated sections, the peak at 1594 cm^{-1} remained the strongest in this region (Figures 4-4 and 4-5), whereas in the corresponding amine spectra it was the peak at 1654 cm^{-1} which remained enhanced. As for the amine treated sections, the peak at 1654 cm^{-1} was assigned to the N-H bending arising from the primary amine, while that at 1594 cm^{-1}, it was the carbonyl stretching vibration in the carboxylate (Tolvaj and Faix, 1995). In the copper-amine treatment the latter vibration was enhanced by the reaction with copper. It was not clear from the FTIR spectra whether the copper carboxylate complex contained amine bound to the copper. Further studies are required to clarify this point. However, the clear reaction of copper with the carboxylic acid functionality strongly supported fixation reactions involving hemicellulose.

It was interesting to note that a small amount of free carboxylic acid (1735 cm^{-1}) was formed during leaching (Figure 4-5). Since this was not observed during leaching of the amine treated wood, it must arise due to copper interaction. This carbonyl stretching vibration was slightly larger for the Cu-DAP and Cu-Polyim sections than for the Cu-MEA, Cu-en, and Cu-AEEA sections. Indeed a small absorption at 1735 cm^{-1} for the carboxylic acid was observed even in the unleached sections (Figure 4-4), suggesting perhaps a lower ability to form copper-amine complexes for these two amines.

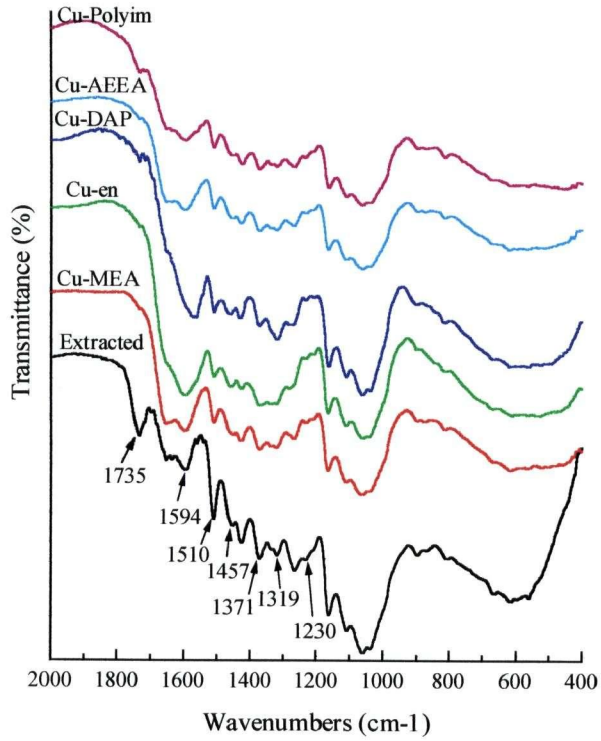


Figure 4-4. FTIR spectra of copper-amine treated southern pine thin sections before distilled water leaching.

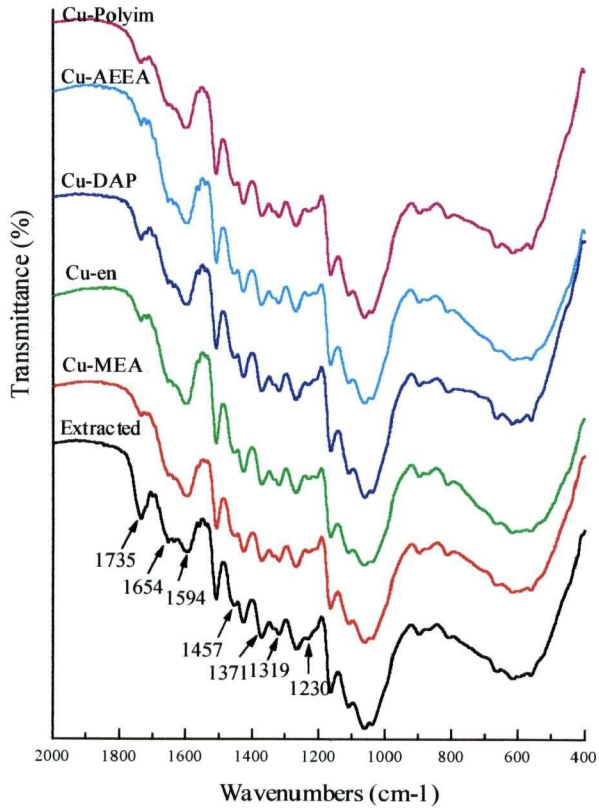


Figure 4-5. FTIR spectra of copper-amine treated southern pine thin sections after distilled water leaching.

4.3.1.3. For copper-HDO amine treated sections

The FTIR spectra of water leached copper-HDO amine treated sections (Figure 4-6) were very similar to those of leached copper-amine treated sections. The peak at 1735 cm^{-1}, assigned to the carboxylic group, was diminished, while the absorption at 1594cm^{-1}, due to the carboxylate stretching vibration, was enhanced. This suggested that formation of copper-carboxylate salts with wood occurred. After water leaching, a small amount of free carboxylic acid functionality was recovered, the evidence for which was the reappearance of the small absorption at 1735 cm^{-1}. This was most easily observed in the CuHDO-Polyim and CuHDO-AEEA treated sections, implying their lower ability to form copper amine complexes with carboxyl acid groups in wood.

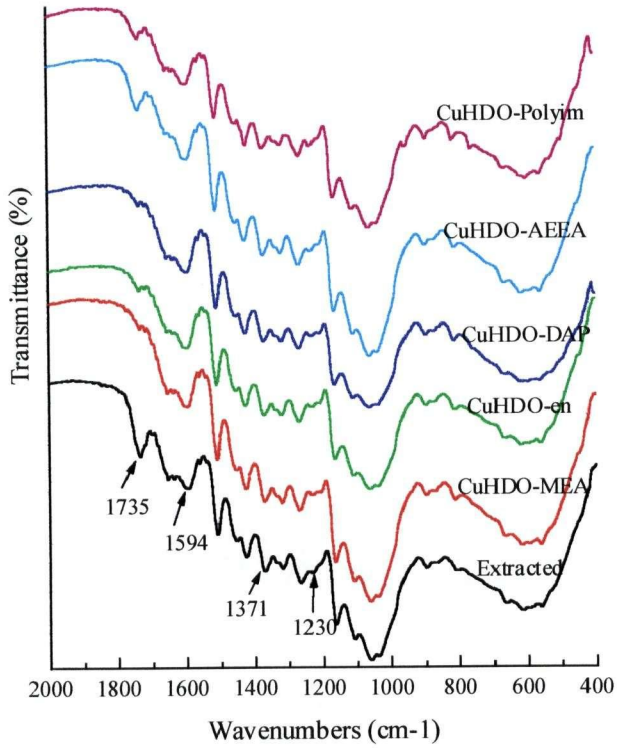


Figure 4-6. FTIR spectra of copper-HDO amine treated southern pine thin sections after distilled water leaching.

Like the copper-amine treated samples, the absorption at 1230 cm^{-1} in the CuHDO.amine treated sections, arising from aryl-alkyl ether linkages in the lignin, was remarkably decreased. This was caused by the loss of the acetal ether linkage in lignin during hydrolysis by the amine. The absorption at 1371 cm^{-1} corresponding to the ring stretching with phenolic O-H bending character (Sarkanen et. al. 1967a) also showed a slight decrease in the leached samples. This was observed in the copper-amine treated samples too. This change could be explained by the activation of the phenolic hydroxyl groups into the phenolate anion under the strong basic conditions, and subsequent reaction of the phenolate anion and copper-amine in the copper-HDO amine solution. The decrease in intensity of peak 1371 cm^{-1} confirmed the interaction between copper-amine species in the copper-HDO amine solution and phenolic hydroxyl groups.

The spectrum of the KHDO treated section (Figure 4-7) showed a decrease in the carboxylate carbonyl stretching peak at 1594 cm^{-1}. KHDO treatment would result in the formation of potassium carboxylate with the carboxylic group in wood, which could be subjected to further hydrolysis reaction in the solution, to completely recover the free carboxylic acid peak at 1735 cm^{-1}, and reduce the carboxylate peak at 1594 cm^{-1}. No changes for either peak 1371 cm^{-1} or 1230 cm^{-1} were observed. This supported the conclusion that it was copper-amine species, rather than free HDO, that was responsible for the changes in FTIR spectra of copper-HDO.amine treated wood. However, FTIR spectra could not clarify whether the $Cu(HDO)_2$ precipitate or phenolate complex contained the HDO bound to copper.

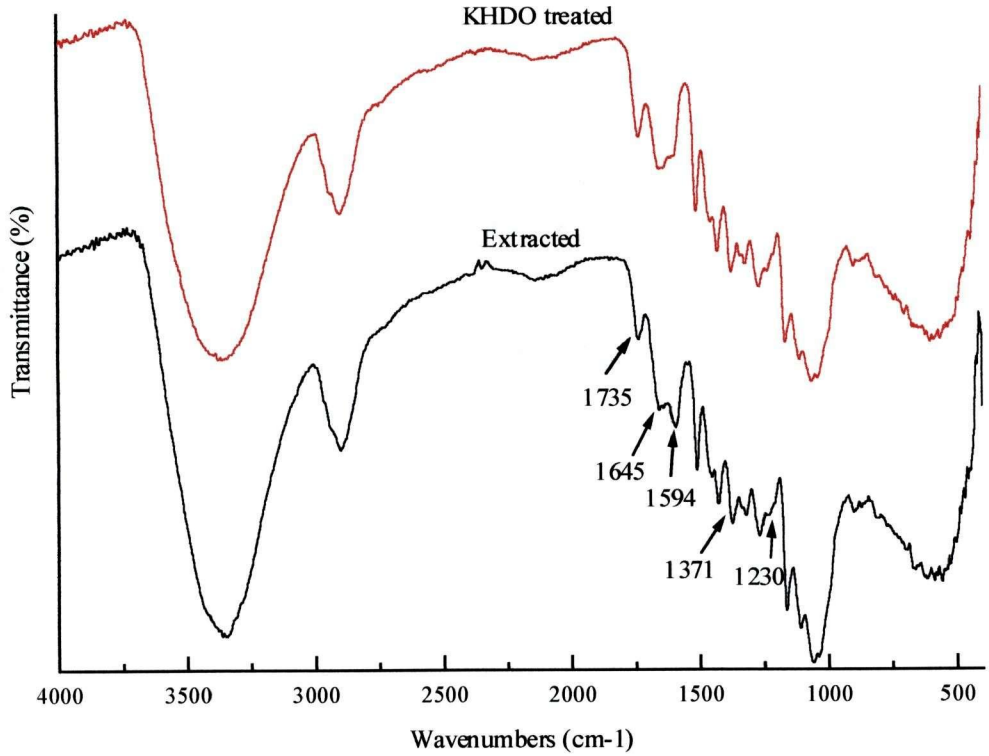


Figure 4-7. FTIR spectra of untreated and a KHDO treated southern pine thin section.

4.3.2 UV-Visible spectroscopy of copper-HDO amine solutions

Comparing the visible spectra recorded for copper-amine solutions with those of copper-HDO amine solutions, it was found that the characteristic peak of latter appeared at the same position as for their corresponding copper-amines (Figure 4-8 and 4-9). This indicated that the same copper species existed in both copper-HDO amine and copper-amine solutions, implying that in copper-HDO amine solutions, the major chemical species present were copper amine and free HDO.

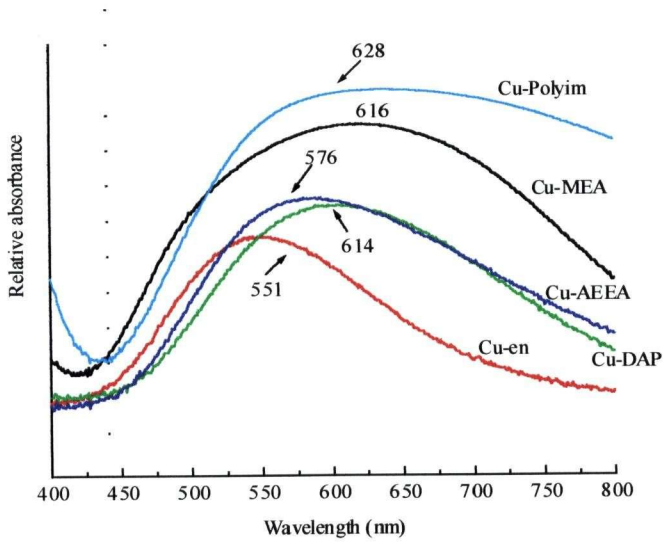


Figure 4-8. UV-Vis spectra of copper amine solution

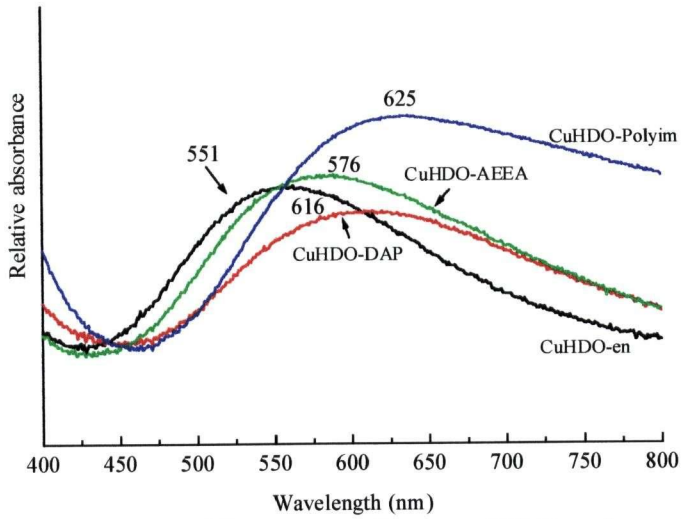


Figure 4-9. UV-Vis spectra of copper-HDO amine solution

4.3.3. XPS spectral analysis

4.3.3.1 The influence of X-ray irradiation on sample stability

During the XPS analysis of several sections the copper spectra suggested the presence of a copper(I) species. To determine whether this arose during fixation or was an artifact of the analysis, pure $[Cu(en)_2(NO_3)_2]$, and a $Cu(en)_2$carbonate treated sapwood section, were exposed to x-ray irradiation for an additional one or two hours, following collection of the initial spectrum. At each time interval, additional spectra were recorded.

In the N1s spectra of solid $[Cu(en)_2(NO_3)_2]$, the reduction of the high energy nitrogen was recognized by the formation of a new peak at a binding energy of ca. 404.0 eV, after prolonged exposure to X-rays (Figure 4-10). It is clear that this new peak arose from the reduction of the nitrate anion, since a) no corresponding reduction of nitrogen in the copper$(en)_2$ carbonate treated section was observed, and b) the binding energy corresponds to that reported for nitrite (Ruddick, 1996). Prolonged exposure during XPS did not cause any significant changes to the C1 and C2 peaks in the C1s spectrum, but a small reduction of the C4 peak was observed (Figure 4-11), resulting in a slight increase in the C3 peak. This suggests that a small amount of C4 type carbon (carbon in a carboxylic acid group) was reduced during the prolonged XPS analysis time.

The Cu2p spectra also showed changes with prolonged exposure during XPS (Figure 4-12). Peaks at 933.65 eV ($[Cu(en)_2(NO_3)_2]$ solid) and 933.03 eV (Cu-en treated wood) increased with longer irradiation time with a concomitant decrease in peaks at 935.63 eV and 934.64 eV, respectively (Table 4-3 and Figure 4-12). Frost et. al. (1972) reported the photo-reduction of copper (II) to copper (I) during XPS analysis. This could

be clearly distinguished by a reduction in the intensity of the satellite peaks (the later arises by simultaneous excitation of the 3d electrons during XPS analysis). The same authors also noted that copper amine compounds seemed to be particularly vulnerable to this reduction. The copper(I) binding energy was reported to be 1-2 eV lower than that of copper(II), and the current measurements support this. The ready reduction of the copper(II) during prolonged analysis in this current study strongly suggests that it arose from XPS analysis and not from the fixation reaction. Low temperature XPS analyses will be necessary to confirm this conclusion. Additional evidence for this conclusion can be drawn from the lack of oxidation products formed in wood (C1s) or amine (N1s) XPS spectra, compared to the reference spectra of untreated wood or pure chemical.

Table 4-3. The binding energies of C1s, N1s and Cu2p and the area ratio of Cu(II) peak to the shake-up satellite peak for copper-amine complexes.

Sample ID	C1s (eV)			N1s (eV)		Cu2p (eV)	
	C1	C2	C3	N1	N2	Cu1	Cu2
$Cu(en)_2(NO_3)_2$		286.36		400.36	407.20	933.65	935.63
Cu-en-Wood	285.00	286.05	288.44	398.53	399.43	933.03	934.64
Cu-Van-NH_3	285.00	286.50	288.00	399.58	400.69	933.28	934.82
Cu-Van-MEA	285.00	286.50	288.00	399.48	---	933.38	934.62

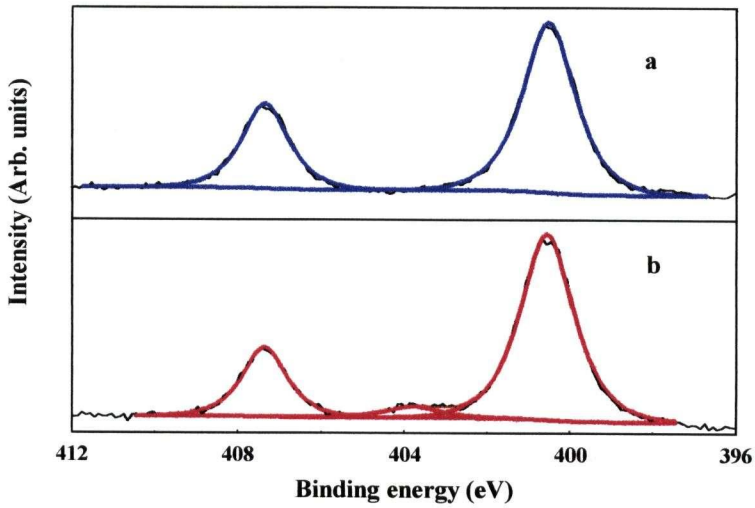


Figure 4-10. XPS N1s spectra of pure $Cu(en)_2(NO_3)_2$, after a) 30 min., and b) 1.5 hrs irradiation.

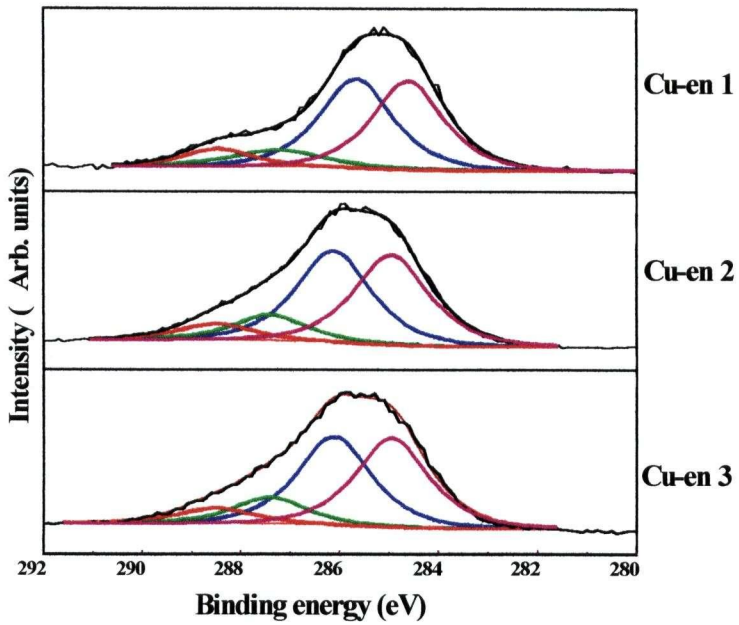


Figure 4-11. XPS C1s spectra of copper-ethylenediamine treated wood after 30 min. (Cu-en1), 1.5 hrs (Cu-en2), and 2.5 hrs irradiation (Cu-en3).

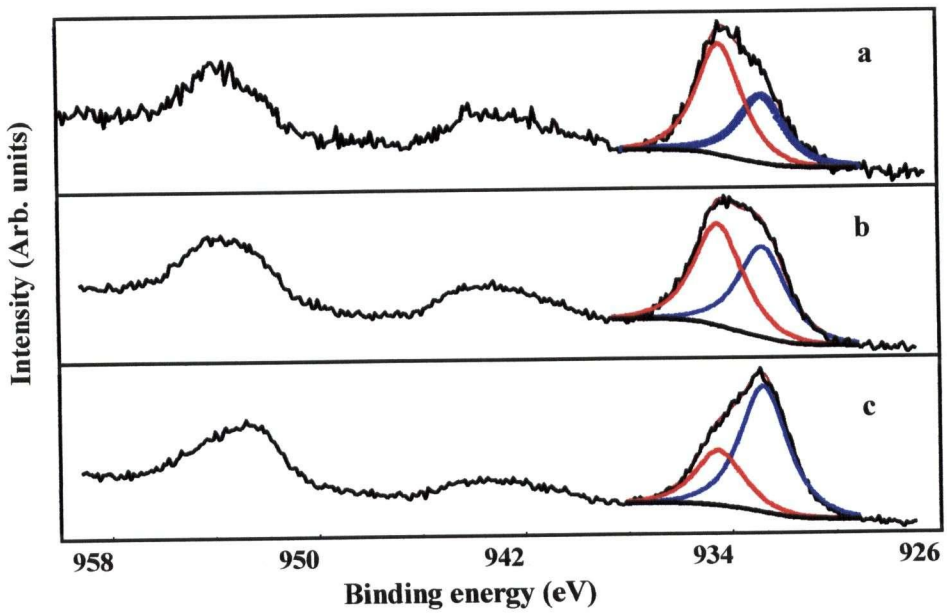


Figure 4-12. XPS Cu2p spectra of copper-ethylenediamine treated wood after a) 30 min., b) 1.5 hrs, and c) 2.5 hrs irradiation.

4.3.3.2 Spectroscopic analysis of pure $Cu(en)_2(NO_3)_2$, $Cu(vanillin)_2(NH_3)_2$, and $[Cu(vanillin)(monoethanolamine)]_2$:

The N1s spectrum of solid $[Cu(en)_2(NO_3)_2]$ showed two single peaks at 400.36 eV and 407.2 eV (Table 4-3, Figure 4-10). The peak at 407.2 eV is in good agreement with that reported for $NaNO_3$ of 407.3 (Folkesson, 1973). Since this molecule lacks a C1 type carbon for referencing the C, N, and Cu, the nitrate nitrogen binding energy at 407.2 eV was used as a reference. The peak with binding energy of 400.36 eV was, therefore, assigned to the primary amine nitrogen. The C1s spectrum showed a clear single peak at 286.36 eV, which was assigned to the C2 type carbon in $[Cu(en)_2(NO_3)_2]$, because of the similar electronegativity of nitrogen and oxygen. The Cu2p spectrum showed two main peaks at 935.63 eV ($Cu2p_{3/2}$) and ca. 956.0 ($Cu2p_{1/2}$) eV (Figure 4-12). Each main peak was accompanied by a broad shake up satellite peak at higher binding energy, which is characteristic for copper(II) compounds. Each satellite was actually comprised of one or two peaks depending upon the type of copper compound (Frost et. al., 1972).

Di(ammine)bis(vanillinato)copper(II) has a distorted octahedral structure, with two nitrogens (ammonia) and two oxygens (phenol) in a square plane around the central copper (Xie et. al., 1995). $[Cu(en)_2(NO_3)_2]$ has a similar distorted octahedral configuration, with four nitrogens (amine) in a square plane around copper (Manriquez, et. al., 1996). The binding energy of nitrogen in the copper-ethylenediamine complex (400.36 eV) was very similar to that recorded for the di(ammine)bis(vanillinato) copper(II) complex (400.69 eV) shown in Table 4-3. Frost et al. (1972) also studied copper$(en)_2$ complexes. For example, for $Cu(en)_2SO_4.H_2O$ they reported a binding energy for the nitrogen of 401.0 eV with a C1s binding energy of 286.8 eV. Adjusting for the

differences in the C2 component of the C1s binding energy, the agreement for the nitrogen peaks was very good. The increase in the nitrogen binding energy for the ethylenediamine in the copper complex from that reported for the free ligand (398.9 eV) by Frost et al. (1972), can be explained by the lower electron density on the nitrogen due to the donation of electrons to the copper.

The reduction of the copper binding energy, when comparing the copper$(en)_2$ nitrate and the di(ammine)bis(vanallinato)copper(II) complex, can be accounted for by the differences in electron donor capacity of nitrogen and oxygen and in the type of bond with copper. As shown by Frost et. al. (1972), increasing the charge on the central copper as in highly polarized molecules like $CuSO_4$ or CuF_2, leads to a higher binding energy for the copper peak. Thus, replacing the highly anionic nitrate by the much less polar vanillato group, will decrease the positive charge on copper, leading to a lower binding energy on copper. This is consistent with the trend shown in Table 4-3 for the nitrated and vanillato complexes. A similar argument can also explain the trend in the copper(II) binding energies for copper nitrate (935.9 eV), reported by Frost et. al. (1972) and the $Cu(en)_2(NO_3)_2$ (935.6 eV) observed here, in that the amine ligand will tend to reduce the positive charge on the copper. As expected the binding energy for copper benzoate of 935.1 eV (after adjustment for differences in C1s carbon (Frost et. al. 1972)) is higher than that for the less polar vanillato complex, but is lower than the more polar copper$(en)_2$ nitrate.

4.3.3.3 Control reference wood samples

As previous studies have reported, the migration of C1 rich extractives to the sample surface can enhance the C1/C2 ratio (Ruddick et al. 1993). This was confirmed in the current study in that after the removal of the extractives with dichloromethane the C1/C2 ratio was significantly lowered (Table 4-4), while the O/C ratio increased. To reduce the confusion during spectral interpretation, the sections were extracted prior to treatment with amine or copper amine solutions.

Table 4-4. O/C ratio and fractional area percent of C1s of amine treated and untreated wood.

Sample ID	O/C	C1	C2	C3	C1/C2
Unextracted	0.42	48.9	41.8	9.2	1.17
Extracted	0.49	38.2	52.6	9.2	0.73
MEAH	0.57	27.6	60.7	11.7	0.46
en	0.49	29.6	58.6	11.8	0.50
en L.	0.55	31.9	55.8	12.3	0.57
DAP	0.49	30.6	56.8	12.6	0.54

4.3.3.4 Amine-treated samples:

The C1s spectra of amine treated sections showed a significantly lower C1/C2 ratio (0.46 to 0.54) than the untreated and extracted wood (Table 4-4). This was due to the addition of C2 type carbon from the amine. After water leaching of the ethylenediamine treated section, the ratio of C1/C2 increased from 0.50 to 0.57, but still remained lower than that in the untreated control (0.73). This confirmed that some amine remained attached to the wood, and supported the interpretation of the FTIR spectra, where an irreversible change in the carboxylate absorption occurred during amine treatment.

Fitting of the N1s XPS spectra of the amine treated sections also confirmed that a small additional peak was present at ca 401 eV (Figure 4-13). The fitting of the N1s spectral envelope was significantly improved (based upon the lowering of the Σ value), when two peaks (designated as N1 and N2) were assigned rather then just one peak. The binding energies for each peak in the amine treated samples were located at ca. 399.8 eV and ca. 401.3 eV (Table 4-5).

The binding energy for N1 was similar to that noted earlier for the pure copper-amine complexes (Table 4-3). It was however, significantly higher than the values reported for uncomplexed amines of 398.1 eV (Nordberg et. al., 1967) and 398.9 eV (Frost et. al., 1972). The increase in the binding energy of the nitrogen over that found in the free amine was proposed to arise from interaction of the amine with the numerous hydroxyl groups found in lignin in wood, and which are known to be activated during treatment with highly basic solutions. This observation could be confirmed by the reduction of the peak at 1370 cm^{-1} in FTIR spectra of amine treated samples.

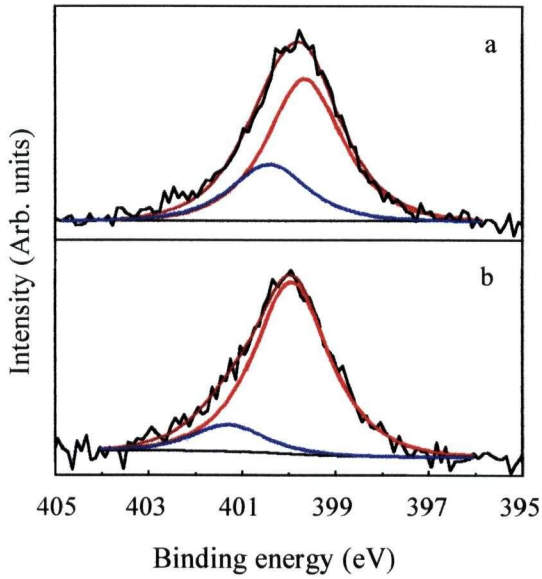


Figure 4-13. XPS N1s spectra of ethylenediamine treated southern pine: a) unleached; b) distilled water leached.

Table 4-5. The binding energies of C1s and N1s spectra for untreated and amine treated samples.

Sample ID	C1s (eV)			N1s (eV)	
	C1	C2	C3	N1	N2
Unextracted	285.0	286.56	288.48		
Extracted	285.0	286.56	288.58		
MEAH	285.00	286.60	288.23	400.09	401.71
en	285.00	286.56	288.27	399.29	401.06
en L.	285.00	286.60	288.30	399.93	401.29
DAP	285.00	286.45	288.32	399.57	401.13

The binding energy for N2 of ca 401.3 eV was significantly higher than nitrogen in a primary amine, and was similar to that reported by Nordberg et al. (1967) for amine-acid salts ($R\text{-}NH_3^+$) of 400.3 to 401 eV. After water leaching of the ethylenediamine treated section, N2 could still be observed, confirming that the amine-acid salts were resistant to water leaching. These findings are consistent with the conclusions from the FTIR data.

The O/C ratio could also provide some support for trends in amine reactions with wood. Torr et al. (1996) used a quantification factor, identified earlier by Dorris and Gray (1978) to interpret changes in the XPS spectra in terms of the molecular changes during acetylation of wood. The area of the XPS peak is related to the concentration of the particular element and the escape depth of the photoelectons that leave the sample. In order to relate the peak areas to actual concentrations of the elements being studied, a machine specific quantification factor must be calculated. This may be determined from

$$A_{O(1S)}/A_{C(1S)} = K \times N_O/N_C$$

Where, Ac = the area of carbon;

Ao = the area of oxygen;

Nc = the number of carbon atom;

No = the number of oxygen atom;

K = the quantification factor.

The data for pure $Cu(en)_2(NO_3)_2$ provided an excellent source for determining the quantification factor, since the exact number of atoms per molecule are known. The ratio of oxygen to carbon in this molecule is 6/4. The ratio of the peak areas was found to be 1.16, so the quantification factor is 1.16 x 4/6 = 0.78. Applying this information to

monoethanolamine produces an O/C ratio of 0.39 (i.e. 0.78 x ½). Thus the addition of monoethanolamine to wood (O/C ratio of 0.49) should cause the O/C ratio to be reduced. This did not happen, indeed the O/C ratio increased during treatment. However, the amine solution was diluted with water. Since amines are much stronger bases than water (being similar to ammonia) in aqueous solution they will tend to form $R\text{-}NH_3^+OH^-$. Thus, when wood was treated with monoethanolamine, it was more appropriate to consider the O/C ratio of 2/2 x 0.78 i.e. 0.78. Thus now the addition of monoethanolamine with an O/C ratio of 0.78 was higher than that of wood (0.49) so that upon treatment the O/C ratio should increase provided the wood surface contains sufficient monoethanolamine. A similar rationale might be used for ethylenediamine but the effect would be smaller since the molecule contains no oxygen atoms. Other factors must also be considered. Since XPS is a surface analysis technique, the distribution of the amine in the thin sections will also affect the ratio.

4.3.3.5. For copper-amine treated samples:

The N1s XPS spectra of copper amine treated samples were best fitted to two peaks, one of which was located around 398.6 eV, while the second and main peak was at a higher binding energy of 399.8 eV (Figure 4-14, Table 4-6). The latter peak was consistent with that observed in amine treated wood, and was also similar to that recorded for copper-amine compounds. The peak at 398.6 eV was in agreement with the values reported for nitrogen in free amine. Thus when copper amine solutions react with wood, some free amine is liberated. Since the ratio of amine to copper is exactly 2:1, this would support the conversion of the bis(amine)copper(II) species present in solution to

aminecopper(II)-wood products, with the release of one amine molecule, or the formation of copper wood products without amine present. The second, and somewhat larger N1s peak at ca. 399.7 eV, was at a slightly lower binding energy than that recorded for pure $Cu(en)_2(NO_3)_2$. It was similar to that for vanillinato-copper(II)-monoethanolamine complex, of 399.48 eV (Table 4-3). The amine was, therefore, clearly involved in forming copper-amine-wood complexes.

Leaching of the copper amine treated samples caused loss of the nitrogen peak (ca. 398.7 eV), due to free amine (Table 4-3). The remaining main nitrogen peak at ca. 399.6 eV was associated with the formation of copper-amine-wood complexes, while a smaller peak at ca. 400.4 eV was possibly assocaited with a hydrolysis reaction of the amine during leaching to produce $R\text{-}NH_3^+OH^-$.

The binding energy for the Cu2p XPS spectrum is a function of the copper oxidation state. The minor shoulder peak at about 933.0 eV was caused by the reduction of copper(II) to copper(I) during XPS analysis. For all copper amine treated sections, the presence of the satellite peak in Cu2p XPS spectra confirmed the formation of copper (II) compounds during its fixation. The assignment of the copper(II) component of the copper ($2p_{3/2}$) peak can be confirmed by comparing the ratio of the copper(II) peak to that of the shake up satellite area (Table 4-6). An almost constant relationship of 1.6 was observed. The copper binding energies of ca. 934.5 eV for the copper-amine treated wood were in good agreement with that recorded for the di(amine)bis(vanillinato)copper(II) complex (934.62 eV), supporting the earlier assignment of the amine binding energy to amine-copper complexes. Indeed, the agreement was rather good considering that in wood, interactions between the wood and the copper would likely cause considerable distortion

of the molecular structure from that present in pure amine-copper complexes. It was also useful to compare the binding energy of the copper in copper-amine treated wood with those reported by Frost et al. (1972). The Cu2p binding energy in $Cu(en)_2SO_4$ was reported to be 935.9 eV (after correction for the binding energy of the C2 carbon in the C1s XPS spectrum). This was almost identical to that reported for copper$(en)_2$(acetate$)_2$, while the comparable value for copper-acetate was 936.3 eV. These values were all higher than those observed in this study for copper-amine treated wood, implying a lower positive charge on the copper, due to bonding to a less polar oxygen atom in wood. This is consistent with reaction of the copper-amine and the guaiacyl groups in lignin. Copper hydroxide and copper carbonate were reported to have binding energies of 937.4 eV and 937.2 eV, respectively (Frost et al., 1972) (based on the C1s spectrum these values are probably too high when converted to a C1 reference of 285.0 eV). It may be concluded that neither of these simple precipitates is formed during fixation of copper amine in wood.

The O/C ratios for the copper-amine treated wood, were all somewhat less than those calculated for amine-treated wood (Table 4-7). This may partly be accounted for by lower amine concentrations used in the copper amine solutions. However, unlike the simple amine treatments, in the copper-amine solutions all of the amine is associated with the formation of amine-copper complexes, and there is no opportunity for association with water. Thus for diamine-copper solutions the O/C ratio is zero, and this will reduce the natural O/C ratio of wood when the copper.amine.wood products are located at the surface (Table 4-7). The reduction was particularly noticeable for the copper polyimine and copper AEEA treated sections. The C1/C2 ratio showed a steady increase in the order

Cu-AEEA ≤ Cu-MEA < Cu-en < Cu-DAP. It would be expected that the AEEAH would lower the ratio the most since it has the highest number of C2 carbons per mole of amine, whereas that for DAP should tend to be the highest, since it is the only amine with C1 type carbon. However, since all of the ratios are greater than that for the wood, other phenomena must be influencing the ratio. For example, the increase in C3 for the Cu-en and Cu-DAP treatment may be compared to a lowering of C3 for the Cu-MEA treatment.

Table 4-6. The binding energies of C1s, N1s and Cu2p and the area ratio of Cu(II) peak to the shake-up satellite peak for copper-amine treated wood.

Sample ID	C1s (eV)			N1s (eV)		Cu2p (eV)		Area ratio of Cu(II) to Satellite
	C1	C2	C3	N1	N2	Cu1	Cu2	
Cu-MEA	285.00	286.22	288.15	398.68	399.78	933.05	934.54	1.5
Cu-MEA L.	285.00	286.66	288.70	399.68	400.48	933.95	935.78	--
Cu-en1	285.00	286.05	288.44	398.53	399.43	933.03	934.64	1.6
Cu-en2	285.00	286.19	287.98	398.42	399.48	932.74	934.43	1.6
Cu-en3	285.00	286.18	287.93	398.35	399.37	932.76	934.52	1.6
Cu-en L.	285.00	286.51	288.31	399.12	400.28	932.81	934.49	--
Cu-DAP	285.00	286.26	288.35	399.08	399.81	932.95	934.39	1.6
Cu-DAP L.	285.00	286.60	288.70	399.64	400.45	933.11		--
Cu-AEEA	285.00	286.02	288.18	398.78	399.74	932.77	934.40	1.7
Cu-Polyim	285.00	285.94	288.01	398.87	399.77	932.43	934.18	1.8

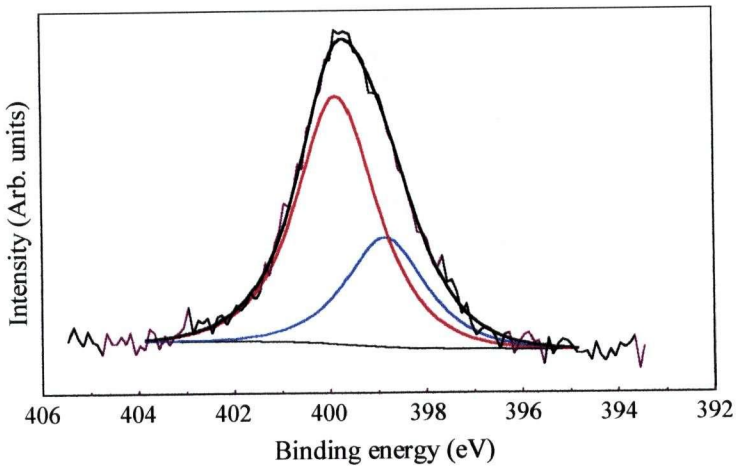


Figure 4-14. XPS N1s spectrum of copper monoethanolamine treated wood.

Table 4-7. O/C ratio and fractional area percent of C1s of amine treated and untreated wood.

Sample ID	O/C	C1	C2	C3	C1/C2
Cu-en Cryst.	1.16	0.0	100.0	0.0	0.00
Cu-Van-NH_3	0.12	79.7	20.3	0.0	3.93
Cu-Van-MEA	0.17	66.8	33.2	0.0	2.01
Cu-MEA	0.46	42.9	48.6	8.5	0.88
Cu-MEA L.	0.59	32.3	59.4	8.3	0.54
Cu-en	0.37	45.0	41.5	13.4	1.08
Cu-DAP	0.39	50.5	38.4	11.1	1.31
Cu-DAP L.	0.49	40.3	52.3	7.5	0.77
Cu-AEEA	0.36	41.0	50.0	9.0	0.82
Cu-Polyim	0.30	43.7	48.0	8.3	0.91

4.3.3.6. For copper-HDO amine treated samples

The N1s spectrum of pure $Cu(HDO)_2$ gave two peaks at 401.98 eV and 402.87 eV due to the non-uniform delocalization of the electrons on the two N atoms in the $Cu(HDO)_2$ molecule (Table 4-8 and Figure 4-15). These two peaks were assigned the characteristic binding energy of nitrogen atoms in solid $Cu(HDO)_2$. Interestingly, the N spectrum of KHDO displayed three peaks at 398.86 eV, 401.11 eV and 402.37 eV (Table 4-8 and Figure 4-15). The two peaks with binding energies of 401.11 eV and 402.37 eV were assigned to the two N atoms in KHDO. The assignment of the small peak at 398.86 eV was uncertain, and it is suspected that this peak was caused by an impurity. The lack of a similar peak in the $Cu(HDO)_2$ spectrum eliminated the possibility of a decomposition product formed during XPS analysis.

Four peaks were recorded for the N1s spectra of CuHDO-en, CuHDO-DAP, CuHDO-AEEA and CuHDO-Polyim treated thin sections (Table 4-8). Two of these peaks at ca. 402 eV and 403 eV can be confidently assigned to the nitrogen from $Cu(HDO)_2$ precipitate based on the XPS spectrum of pure $Cu(HDO)_2$. The peak at ca. 399.9 eV is consistent with that recorded for copper-amine treated wood, and was assigned to amine bound to copper. The fourth peak at the lowest binding energy of ca. 399 eV was similar to that found in free amine. For CuHDO-en and CuHDO-DAP treated sections, two of the largest peaks, were those at 402 eV and 403 eV, indicating that in these treatments the predominant copper species fixed in wood was $Cu(HDO)_2$. The formation of the highly stable $Cu(HDO)_2$ precipitate could be achieved by neutralizing the copper-HDO amine with the acidic protons present in wood. The CuHDO-en treated

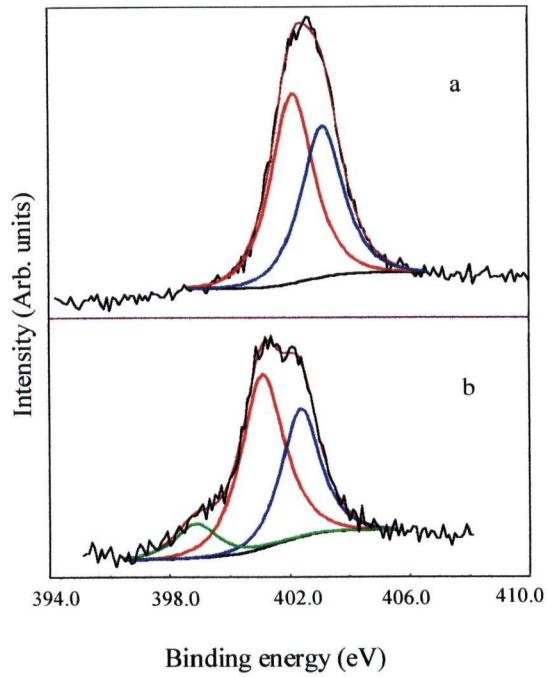


Figure 4-15. XPS N1s spectra of a) $Cu(HDO)_2$ and b) KHDO.

Table 4-8. The binding energies of C1s, N1s and Cu2p for pure $Cu(HDO)_2$ and KHDO, and copper-HDO amine treated samples.

Sample ID	N1s (eV)				Cu2p (eV)	
	N1	N2	N3	N4	Cu1	Cu2
Pure $Cu(HDO)_2$			401.98	402.87	933.38	935.86
KHDO solid	398.86		401.11	402.37		
CuHDO-en	399.11	399.97	402.01	403.20	933.04	935.55
CuHDO-en L.		400.08				
CuHDO-DAP	399.12	400.19	401.91	402.88	932.74	935.27
CuHDO-AEEA	399.15	399.79	401.95	403.00	932.72	934.57
CuHDO-Polyim	398.91	399.66	401.25	402.84	932.39	934.39

sample also showed a large peak at 399.97 eV, assigned to nitrogen in copper-amine wood complexes. This implied that copper-amine wood reaction products were also significant in the CuHDO-en treatments. In the CuHDO-DAP spectrum, the corresponding peak at 400.19 eV was much smaller, suggesting that much less copper-amine wood complex was formed in CuHDO-DAP treated sections. The smallest of the four peaks in CuHDO-en and CuHDO-DAP treated sections was located at ca.399 eV and arose from excess free amine. After water leaching of the CuHDO-en treated sample, the free amine was washed away, resulting in the loss of the peak at 399 eV. In addition, the peaks due to $Cu(HDO)_2$ precipitate on the wood surface, were also lost. Only the peak of 400.08 eV related to the copper-amine wood complex remained. Since XPS is a surface analysis technique, the loss of the $Cu(HDO)_2$ precipitate on the section surface during washing, would result in it not being detected during XPS analysis.

For CuHDO-AEEA and CuHDO-Polyim treated samples, the N1s spectra were different from those of CuHDO-en and CuHDO-DAP. The main peaks were located at ca. 399.0 eV and 399.7 eV. The latter peak was consistent with that assigned to copper-amine-wood complex, implying that the formation of copper-amine complex with wood was the major product during the fixation. The peak at ca. 399.0 eV was related to the presence of free amine. Since the mole ratio of amine to copper in CuHDO-AEEA and CuHDO-Polyim treating solutions was much higher (5:1) than that in either CuHDO-en or CuHDO-MEA (2:1), the peak due to free amine became predominant. Conversely, in CuHDO-AEEA and CuHDO-Polyim treated samples, the corresponding nitrogen peaks arising from $Cu(HDO)_2$ precipitate, only contributed to a minor peak area, indicating that the formation of $Cu(HDO)_2$ precipitate in wood was much less important. This could be

the reason for the low leaching resistance for these two treatments compared to the diamine HDO solutions (Chapter 3). For all the copper-HDO amine treatments, no nitrogen from free HDO (401.11 eV recorded in KHDO) was found.

As discussed previously (Section 4.3.2.5), the presence of the satellite peak in Cu2p XPS spectra confirmed the presence of copper(II) compounds although some reduction of the copper occurred during the XPS measurement. In pure $Cu(HDO)_2$ solid, the copper binding energy was 935.86 eV. In CuHDO-en and CuHDO-DAP treated wood, the copper binding energy of ca. 935.5 was in good agreement with that recorded in $Cu(HDO)_2$ solid, confirming the dominant formation of $Cu(HDO)_2$ precipitate in wood. For CuHDO-AEEA and CuHDO-Polyim treatment, the lower copper binding energy at ca.934.5 eV was consistent with that found in the copper-amine-wood complex (Table 4-6). This provides further evidence that for CuHDO-AEEA and CuHDO-Polyim, the formation of a copper amine complex with wood was more predominant during fixation, than the formation of $Cu(HDO)_2$.

4.3.4. ESR spectral analysis

4.3.4.1. Copper-amine treated samples

The most common molecular geometry for copper(II) is that the ligands bonded to copper(II) are arranged in a distorted octahedral environment with four ligands around the central copper ion in an approximate plane. The copper-ligand bond lengths for these four ligands are shorter than the remaining copper-ligand bonds perpendicular to the plane. The perpendicular bonds involve d_z^2 orbitals on copper and play only a minor role in both magnetic and optical properties of the copper complex (Peisach and Blumberg, 1974).

The hyperfine splitting, $A_\perp$, arising from the interaction of the nuclear magnetic moment of the Cu^{2+} at $g_\perp$, is usually very small, so that this feature of the spectrum often shows no splitting. On the other hand, $A_{//}$, the nuclear hyperfine splitting at $g_{//}$, is usually much larger. The magnitudes of $A_{//}$ and $g_{//}$, which are dependent on the nature of the ligands attached to Cu^{2+}, have often been used to assign the structure. Vanngard (1972) compiled $g_{//}$ and $A_{//}$ for a series of model compounds and proteins, and suggested that the values of $g_{//}$ and $A_{//}$ varied with the composition of the ligand atoms bound to the copper. They also suggested that ESR might be employed to define the structural geometry of the copper in the copper proteins. Table 4-9 summarizes the relationship of $g_{//}$ and $A_{//}$ in different copper compounds bound to oxygen and/or nitrogen. The general trend for the changes of $g_{//}$ and $A_{//}$ indicates that the $g_{//}$ value becomes smaller as the number of nitrogen atoms bonded to the copper increases, and the $A_{//}$ increases.

Table 4-9. The relationship between the magnetic parameters of $g_{//}$ and $A_{//}$ for a series of copper(II) compounds.

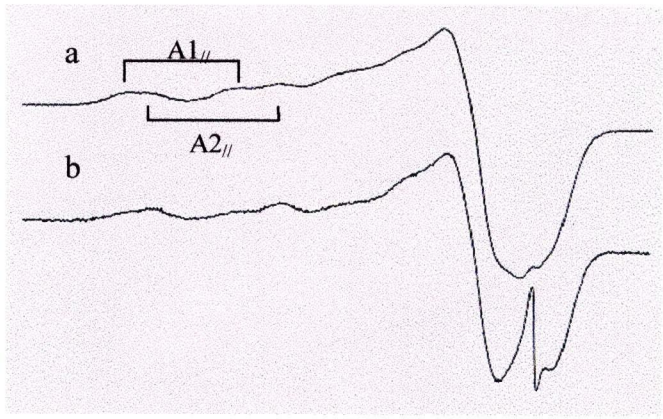
Copper compounds	$g_{//}$	$A_{//}$ (x 10^{-4} cm^{-1})
4O*	2.37	132
4O**	2.41	135
1N3O**	2.36	142
2N2O*	2.27	166
2N2O**	2.26	173
3N1O**	2.24	176
4N*	2.21	197
4N**	2.21	196

* Recorded by Ruddick, 1992.
** Recorded by Peisach and Blumberg, 1974.
4O: copper bond to 4 oxygen in the plane.
1N3O: copper bond to 3 oxygen and 1 nitrogen in the plane.
2N2O: copper bond to 2 oxygen and 2 nitrogen in the plane.
3N1O: copper bond to 1 oxygen and 3 nitrogen in the plane.
4N: copper bond to 4 nitrogen in the plane.

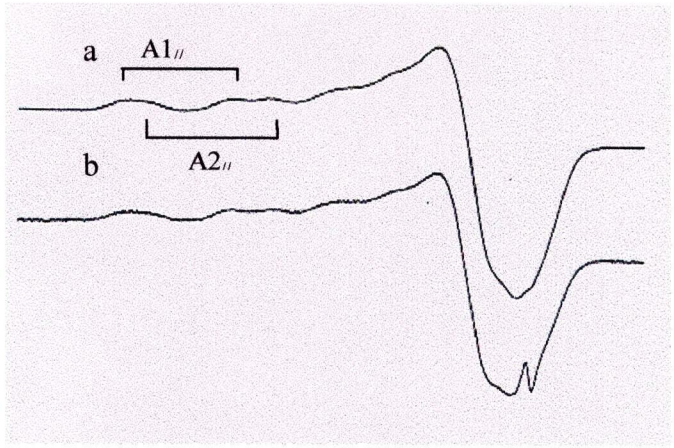
The four peaks arising from hyperfine splitting in the $g_{//}$ area for all copper amine treatments are clearly observed. In addition, the spectra of diamine copper treated samples showed that at least two different copper species were present, as two sets of peaks were clearly visible in water leached treated wood (Figure 4-16). After citrate buffer leaching, the two copper species remained, but the shoulder peak at $g_{\perp}$ area increased, implying that the copper species giving rise to the signal at the higher field is fixed to a greater extent (Figure 4-16). For Cu-MEA and Cu-Polyim treatments, the four

hyperfine induced peaks could be seen, but the quality of the spectra was poorer and the two sets of peaks in $g_{//}$ area would not be distinguished, although the shoulder peak at $g_{\perp}$ area increased during buffer leaching (Figure 4-17). It is known that weak broad lines will occur if the copper concentration is too high (Parish, 1990). This might be the reason that Cu-MEA and Cu-Polyim treatments generated poor hyperfine structures at the low field region. The leaching study showed Cu-MEA and Cu-Polyim treated wood had the highest copper remaining after both water and buffer leaching.

The ESR spectral parameters for copper-amine treated wood after leaching are given in Table 4-10. The electronic data is typical for the square plane, six coordinate, Cu(II) complexes with a d_x^2-d_y^2 ground state. The understanding of the nature of the ligand interactions in these copper complexes requires closer examination of the electronic parameters g and A (Sakaguchi and Addison, 1979). Assuming all the copper species have the same molecular structure, the values of $g_{//}$ and $A_{//}$ for the Cu-MEA and Cu-Polyim treatments are in agreement with a central copper anion complexed to two nitrogen atoms from the amine ligands and two oxygen atoms from wood or amine. This finding confirms the conclusion from the leaching study that one of the predominant copper complexes after leaching is one mole of copper bonded to two moles of amine. Similar electronic parameters were found after buffer leaching, suggesting that the copper-nitrogen wood complex is stable in the citrate buffer solution.

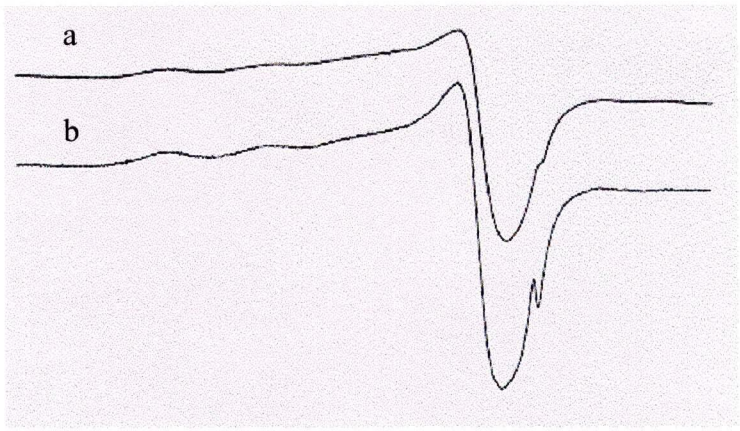


Cu-en
treated

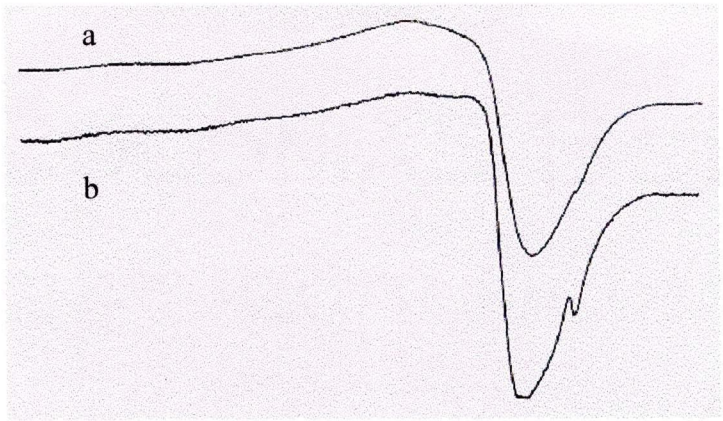


Cu-AEEA
treated

Figure 4-16. ESR spectra of copper-diamine treated wood. a) water leached; b) citrate buffer leached. $A1_{//}$: $A_{//}$ for copper species (1); $A2_{//}$: $A_{//}$ for copper species (2).



Cu-MEA
treated



Cu-Polyim
treated

Figure 4-17. ESR spectra of copper monoamine treated wood. a) water leached; b) citrate buffer leached.

Table 4-10. ESR spectral parameters of $g_{//}$ and $A_{//}$ for copper-amine treated wood after water and citrate buffer leaching.

Sample ID	$g_{//}$	$A_{//}$ ($x10^{-4}cm^{-1}$)
Cu-MEA-water	2.256	172
Cu-MEA-buffer	2.250	173
Cu-en-water (1)	2.250	176
Cu-en-water (2)	2.195	206
Cu-en-buffer (1)	2.236	183
Cu-en-buffer (2)	2.194	198
Cu-DAP-water (1)	2.241	176
Cu-DAP-water (2)	2.214	190
Cu-DAP-buffer (1)	2.253	173
Cu-DAP-buffer (2)	2.216	194
Cu-AEEA-water (1)	2.245	178
Cu-AEEA-water (2)	2.199	198
Cu-AEEA-buffer (1)	2.251	174
Cu-AEEA-buffer (2)	2.200	194
Cu-Polyim-water	2.259	170
Cu-Polyim-buffer	2.253	172

For diamine copper treatments, two different copper species were present in treated wood after fixation. One of the copper species (1) has relatively higher $g_{//}$ value, but smaller $A_{//}$ value. The $g_{//}$ and $A_{//}$ values are similar to those for copper bound to two or three nitrogen atoms (Table 4-9). The second copper species (2), which had a lower $g_{//}$ and higher $A_{//}$, is consistent with the values reported for copper bound to four nitrogen atoms (Table 4-9). Nitrogen is more electron rich than oxygen and this is reflected in larger values of $A_{//}$ and small values of $g_{//}$ (Peisach and Blumberg, 1974). This again confirmed the presence of copper bound to two amines in the treated wood. After buffer leaching, the signal of copper species (1) was relatively decreased to that of copper (2), implying that the copper complexed with two amines to wood, is more stable than the other copper species during buffer leaching.

However, the ESR spectrum did not provide evidence the formation of copper wood complex without amine being present, although the leaching study confirmed its presence. The reason for the absence of copper species complexed only to wood in the ESR spectrum is not very clear. It is possible that copper(II) occurred in a tetrahedral coordination when complexed to wood. This will result in the line broadening, which is often sufficient to obscure any quadrupole interaction with the copper neclei (Parish, 1990).

4.3.4.2. For copper-HDO amine treated samples

The ESR spectral parameters for copper-HDO amine treated samples are listed in Table 4-11. For CuHDO-Polyim treated wood, two copper species were found in the ESR spectra. Copper species (1) has lower $A_{//}$ and higher $g_{//}$, which is consistent with two

nitrogen atoms and two oxygen atoms complexed to the Cu(II) atoms in a distorted octahedral environment (Table 4-9). Copper species (2) generated similar $g_{//}$ and $A_{//}$ values compared to the other treatments (CuHDO-en, CuHDO-DAP, and CuHDO-AEEA), all of which had very similar values of $g_{//}$ and $A_{//}$. However, the values of $g_{//}$ and $A_{//}$ are not in good agreement with those recorded for the $Cu(HDO)_2$ solid in DMSO. This may be due to some residual effect of the amine on the precipitated $Cu(HDO)_2$. It is also possible that the $g_{//}$ and $A_{//}$ values for $Cu(HDO)_2$ in DMSO solution may not reflect the actual bond geometry of copper in $Cu(HDO)_2$ solid.

Apart from the CuHDO-Polyim treated sawdust, there are no signs of other copper-amine species present in copper-HDO amine treated wood. This is surprising, since the XPS study indicated that for both CuHDO-AEEA and CuHDO-Polyim, the copper-amine-wood reaction was dominant. The reason for the difference is not clear. Key differences between the experimental procedures for the XPS and ESR were the use of earlywood thin sections for the former, and leached solid wood blocks for the latter.

Table 4-11. ESR spectral parameters of $g_{//}$ and $A_{//}$ for copper-HDO amine treated wood after water and citrate buffer leaching.

Sample ID	$g_{//}$	$A_{//}$ ($x10^{-4}cm^{-1}$)
$Cu(HDO)_2$ in DMSO	2.258	176
CuHDO-en-water	2.213	185
CuHDO-en-buffer	---*	---
CuHDO-DAP-water	2.228	182
CuHDO-DAP-buffer	---	---
CuHDO-AEEA-water	2.222	188
CuHDO-AEEA-buffer	2.225	188
CuHDO-Polyim-water (1)	2.219	172
CuHDO-Polyim-water (2)	2.246	176
CuHDO-Polyim-buffer (1)	2.197	170
CuHDO-Polyim-buffer (2)	2.249	174

* No hyperfine structure.

4. 4. Conclusions

Amine treatment of thin southern pine sapwood sections caused the irreversible removal of the carboxylic acid groups. The FTIR and XPS spectra were supportive of an amine-acid salt formation that resisted leaching. Two nitrogen peaks could be observed in the XPS spectra, consistent with an amine acid salt, and an amine which was also reacted with the wood lignin.

The copper-amine treatments also caused the loss of the carboxylic acid functionality, although in this case the nitrogen XPS did not support the formation of an amine acid salt, but rather suggested that the amine was bound to copper as well as reacting with wood. From both the FTIR and XPS spectra it may be concluded that the copper-amine treatments react primarily with the lignin and hemicellulose components. The XPS spectra also showed that the copper-amine compounds, both in pure form as well as in treated wood, were relatively easily reduced during spectral analysis with the formation of copper(I). However, there was no evidence that this was occurring during fixation.

FTIR spectra of copper-HDO amine treated samples are very similar to those of the copper-amine treatment. Whether $Cu(HDO)_2$ precipitated or the copper formed a phenolate complex containing HDO can not be clarified by FTIR analysis. XPS measurements were able to confirm the formation of $Cu(HDO)_2$ precipitate in the copper-HDO amine treated wood. It was found by XPS, that the dominant fixation reaction in CuHDO-en, CuHDO-DAP treated samples was the precipitation of $Cu(HDO)_2$ solid. For CuHDO-AEEA and CuHDO-Polyim treatments, the formation of copper-amine wood

complex was more important during the fixation. However, the XPS was unable to determine whether diamine-copper(II) or amine-copper(II) compounds were formed in wood.

The ESR spectra provided valuable evidence on which copper complexes were formed in the treated wood after fixation. For copper amine treatments, the dominant copper complexes are those with two moles of amine and one mole of copper. For copper-HDO amine treatments, ESR data suggested the formation of $Cu(HDO)_2$ precipitate during fixation. However, copper complexes with one or two moles of amine are also likely formed in copper-HDO amine treated wood. In the CuHDO-polyim treatment, a second signal was observed, indicative of a copper amine wood reaction product, which had a amine : copper mole ratio of 2:1.

Chapter 5

Reactions of vanillin, a lignin model compound with copper-HDO monoethanolamine and copper ethylenediamine sulphate solutions

5.1. Introduction

Compared to the popular chromated copper arsenate (CCA), ammoniacal copper preservatives possess a significant advantage when treating refractory wood species, because of their improved penetration (Rak, 1997 and Ruddick, 1980). However, the evaporation of the volatile ammonia from the solvent during drying of the treated timber can lead to the formation of water-insoluble copper salts on the wood surface. This is undesirable when the treated wood is used in residential construction, where appearance is a major consideration. An alternative approach, that can overcome this problem, is to solubilize the copper with an amine. Fixation of the copper-amine in wood thus depends on the reaction of wood protons with the copper-amine complexes present in solution, leading to insoluble copper compounds formed in the wood. However, the nature of these complexes remains unknown.

With increasing awareness of the need to minimize the environmental impact of treated wood, there is great interest in better understanding the fixation chemistry of copper-amine preservatives. Several reactions are possible. These include: a) the formation of copper-amine complexes with wood components, such as lignin, hemicellulose, and heartwood extractives; b) the formation of simple copper complexes

with wood, which do not contain amine; and c) the precipitation of copper compounds in wood during the reaction with other co-biocides (Ruddick, 1996). The validity of the hypothesis has been partially demonstrated by several researchers. In particular, a previous study has shown that copper ethanolamine can form a stable compound with the lignin model compound, vanillin (Ruddick et. al., 2000). The copper-ethanolamine-vanillin complex was found to be a dimeric pyramidal structure. This confirmed that when wood is treated with copper ethanolamine solution, a stable lignin-copper-ethanolamine complex can be formed. ESR studies by Ruddick (1992) and Hughes et. al. (1994) suggested that the copper amine complexes are bound to wood through oxygen from the wood, while other spectroscopic investigations (Jiang and Ruddick, 1999; Kamdem and Zhang, 2000; Thomason and Pasek, 1997; Zhang and Kamdem, 2000) identified reactions between copper and lignin or hemicellulose as being potentially important. It must be noted that while these studies support the reaction pathway in which a copper-amine lignin or hemicellulose complex is formed during fixation, this does not eliminate the possibility of other fixation reactions occurring. Indeed studies on the leachability of copper amine treated wood support several copper compounds being formed (Jiang and Ruddick, 2000).

In order to better understand the nature of the interactions between wood and copper-amine preservatives, as well as the function of the co-biocide HDO during the fixation process, the reactions of vanillin (a lignin model compound) with copper ethylenediamine and copper-HDO monoethanolamine were investigated. Vanillin was used to imitate the abundant guaiacyl units of lignin in wood, to investigate the possible

reaction between lignin and copper amine solutions. Guaiacyl units dominate (80-90%) the basic lignin building block of softwood lignin (Sjostrom, 1992). Following the formation of the crystalline solids, FTIR, ESR, and x-ray crystallography were used to characterize the product compounds.

5.2. Materials and methods

5.2.1. Reaction of vanillin with copper-HDO monoethanolamine sulpate solution

An aliquot (2.416 g, 0.0396 mol) monoethanolamine was added to 20 ml copper sulphate solution (0.824g, 0.0033mol $CuSO_4.5H_2O$) in distilled water. After stirring to ensure complete dissolution, 0.664g (0.0033mol) $KHDO.H_2O$ was added to form a clear solution of copper-HDO monoethanolamine with the mole ratio of Cu: HDO: MEAH of 1:1:12. This solution was then added drop-wise to 100 ml of a 0.0066 molar vanillin solution (1g vanillin in 100 ml warm distilled water). The solution was allowed to stand on the bench for several days during which purple crystals were formed. The crystals were carefully filtered, washed with distilled water to remove the unreacted chemicals, and air-dried at room temperature.

The infrared spectrum of the purple crystals was recorded using a Perkin-Elmer 1600^{TM} spectrophotometer. The solid was ground and mixed with dry KBr and compressed into a pellet. The spectrum was acquired using 4 scans, at resolution 4 cm^{-1}, over the wavenumber range of 400-4000 cm^{-1}. For comparison a technical sample of $Cu(HDO)_2$ powder was prepared in the same way for FTIR measurement.

5.2.2. Reaction of vanillin with copper ethylenediamine sulphate solution

5.2.2.1. Reaction of vanillin with copper ethylenediamine sulphate solution

Vanillin (1g, 0.0066mol) was dissolved in 100ml distilled water. Ethylenediamine (0.238g, 0.00396 mol) was added to 20 ml copper sulphate solution (0.824g, 0.0033 mol

$CuSO_4.5H_2O$ in distilled water) to form the copper ethylenediamine (Cu-en) solution with the mole ratio of Cu to ethylenediamine of 1: 1.2. The Cu-en solution was then added dropwise to the vanillin solution which was stirred during the addition. The solution was allowed to stand at room temperature for several days. Several reactions occurred during which a red crystalline precipitate was formed. The red crystals were carefully filtered, washed with distilled water to remove the unreacted chemicals, and vacuum dried at room temperature. A single crystal of the copper-vanillin complex was obtained through careful recrystalization in a dilute vanillin-copper-ethylenediamine solution.

5.2.2.2. Analysis of the red crystalline solid

The FTIR spectrum of the red solid was recorded as a KBr pellet on a Perkin-Elmer 1600 spectrophotometer™, using 4 scans, at a resolution of 4 cm^{-1}, over the wavenumber range of 400-4000 cm^{-1}. A 0.05g aliquot of the red crystalline solid was dissolved in 10 ml dimethylsulphoxide (DMSO) for ESR examination. The ESR spectrum of the crystalline sample in DMSO solution was collected by a Bruker ECS 106™ spectrometer equipped with a variable temperature unit, operating at a frequency of 9.60 GHz (X-band) and 50 KHz field modulation. The carbon, hydrogen and copper elemental analysis of the crystalline compound was carried out by the Canadian Microanalysis Company, Ladner, B.C.

5.2.2.3. X-ray crystal structure determination

The X-ray single crystal structure analysis was performed using a Rigaku AFC6S diffractometer. All measurements were made on a CCD area detector with graphite monochromated Mo-Kα radiation. The crystal data and details of the data collection are summarized in Table 5-1. Of the 7086 reflections which were collected, 1916 were unique (R_{int} = 0.036); equivalent reflections were merged. Data were processed using the d*TREK™ program, and corrected for Lorentz and polarization effects.

The structure was solved by heavy-atom Patterson methods and expanded using Fourier analysis techniques (Beurskens et. al. 1992). The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, the rest were included in fixed positions. The final cycle of full-matrix least-squares refinement was based on 1798 observed reflections ($I > 3.00\sigma(I)$) and 122 variable parameters. Neutral atom scattering factors were taken from Cromer and Waber (1992). Anomalous dispersion effects were included in F_{calc} (Ibers et. al., 1964), and the corrections were taken from the International Tables for X-ray Crystallography (Creagh and Hubbell 1992). The values for the mass attenuation coefficients are those of Creagh and Hubbell (1992). All calculations were performed using the *teXsan*™ crystallographic software package of Molecular Structure Corp.™

Table 5-1. Crystallographic data and details of the structure determination.

Compound	$(C_8H_7O_3)_2Cu(H_2O)_2$
Empirical Formula	$C_{16}\ H_{18}\ Cu\ O_8$
Formula Weight	401.86
Crystal System	Monoclinic
Space group	C2/c (#15)
a, [Å]	21.989(1)
b, [Å]	10.5802(5)
c, [Å]	7.6964(4)
α, [deg]	90
β, [deg]	105.026(4)
γ [deg]	90
V [Angstorm]	1729.3(2)
Z	4
$D_{(obs)}$, $D_{(calc)}$ [g/cm^3]	0.000, 1.421
F(000)	828
Mu(MoKa) [/mm]	1.3
Crystal Size [mm]	0.30 x 0.40 x 0.40
Temperature (K)	173
Radiation [Angstrom]	MoKa 0.71070
Theta Min-Max [Deg]	3.7, 28.0
Scan (Type & Range) [Deg]	Phi & Omega, 0.5
Dataset	-25: 25 ; -12: 13 ; -9: 10
Tot., Uniq. Data, R(int)	7086, 1916, 0.036
Observed data [I > 2.0 sigma(I)]	1798

5.3. Results and discussion

5.3.1. Reaction of vanillin with copper-HDO monoethanolamine sulphate solution

The FTIR spectra of the purple crystalline solid produced from the reaction of vanillin with copper-HDO monoethanolamine sulphate solution and the pure $Cu(HDO)_2$ are compared in Figure 5-1. It is clear from this comparison that the compounds are identical, in that the key differences in the spectra (peaks at 3432 cm^{-1} and 1650 cm^{-1}) can

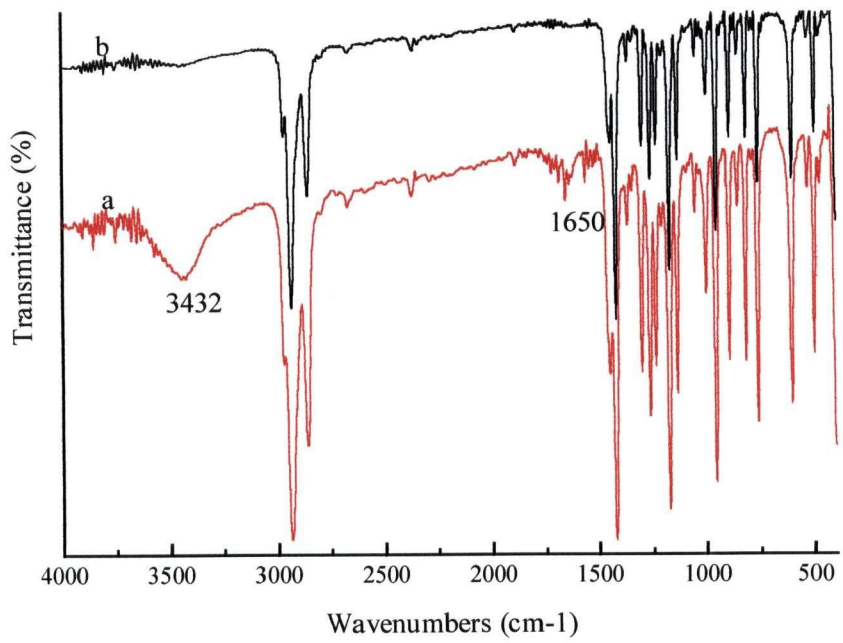


Figure 5-1. FTIR spectra of (a) $Cu(HDO)_2$ and (b) purple crystalline solid from the reaction of vanillin and copper-HDO monoethanolamine solution.

be assigned to the presence of free ligand in the technical grade $Cu(HDO)_2$. Thus the product resulting from the reaction of copperHDO.monoethanolamine with vanillin is copper$(HDO)_2$. The ready formation of copper$(HDO)_2$ in preference to an amine-copper-vanillin product, reflects the very stable nature of the copper compound. It may be anticipated that reactions involving the HDO ligand may tend to be dominated by precipitation rather than formation of copper-amine wood complexes. The crystal structure of $Cu(HDO)_2$ has been reported by Klebe et. al. in 1996.

5.3.2. Reaction of vanillin with copper ethylenediamine sulphate solution

Reaction of copper ethylenediamine sulphate solution with vanillin produced a red crystalline solid. The red crystals, that were insoluble in either water or common organic solvents such as ethanol and methanol, were slightly soluble in DMSO. The elemental analysis of this red vanillin-copper complex was follows: C, 48.27%; H, 4.29%; Cu, 14.6%. This corresponded to $C_{16}H_{18}O_8Cu$ which requires: C, 47.8%; H, 4.5%; Cu, 15.8%. No nitrogen could be detected, indicating that no amine was present in the complex.

5.3.2.1 X-ray structural examination

The structure of the complex determined by X-ray crystallography is comprised of a central copper(II) bonded to two vanillin and two water molecules. The perspective view of the complex with the numbering system is shown in Figure 5-2. In this copper complex, both the methoxyl and phenolic oxygen atoms of each guaiacyl unit coordinate

to the central copper, together with oxygen atoms from two water molecules, to form a six coordinated copper molecule. The atomic coordinates and equivalent isotropic thermal parameters are presented in Table 5-2, while the inter-atomic bond distance and angles are listed in Tables 5-3 and 5-4, respectively.

The copper atom displays a distorted octahedral coordination with two-fold symmetry. The two methoxyl oxygen atoms from vanillin together with the two oxygen atoms from the water, form an approximately square-planar arrangement with the central copper. The Cu-O (methoxyl) bond length of 2.255 Å is longer than that of the Cu-O (water) bonding of 2.082 Å. The latter bond length, is similar to, but slightly smaller than, the value of 1.976 Å reported by Manriquez et. al. (1996) for the $[Cu(en)(H_2O)_2]SO_4$. The two Cu-O (water) bonds are cis oriented in the plane. The Cu-O (methoxyl) bond distance of 2.255 Å is similar to the 2.317 Å found previously by Greenhough and Ladd (1978) for the bis(vanillato)(N,N,N',N'-tetramethylethylenediamine)copper(II), and 2.371 Å reported by Xie et. al. (1995) for di(ammine)bis(vanillato)copper(II).

The very distorted octahedral configuration around the central copper is completed by the axial phenolic oxygen atoms at the Cu-O (phenolic) of 1.911 Å from the copper, and at an angle about 77° to the plane. This Cu-O bond distance of 1.911 Å can be compared to those reported by Xie et. al. (1995) of 1.969 Å, and 1.941 Å for di(pyridine)bis(vanillato)-copper(II)monohydrate described by Hobson et. al. (1973). The current copper complex, has a structure that is very similar to that of the red isomer of bis(4-formyl-2-methoxylphenolato)(N,N,N',N'-tetramethylethylenediamine)copper(II). In the two complexes the methoxyl oxygen atoms in the vanillin are both in-plane and cis,

while the $Cu\text{-}O_{axial} < Cu\text{-}O_{in\text{-}plane}$. The axial phenolic oxygen atoms complete the coordination configuration at a distance of 1.901 Å from the copper (Greenhough and Ladd, 1978).

In each unit cell hydrogen bonding occurs between the two adjacent complexes through the formyl and phenolic oxygen atoms in vanillin and the hydrogen atoms from the water (Table 5-5). The hydrogen-oxygen inter-molecular bond distances range from 2.06 to 3.11 Å. The close contacts for the phenolic oxygen and the water oxygen is 2.946 Å which is similar to that reported for the hydrogen bonding detected in di(pyridine)bis(vanillato)-copper(II)monohydrate (Hobson et. al., 1973). This strong hydrogen bonding arises from the delocalization of electrons to the carbonyl oxygen from the conjugated benzene ring, resulting in greater electronegativity on the oxygen atoms. A packing diagram has been depicted in Figure 5-3. This structure clearly confirms that copper can form stable water-insoluble compounds with vanillin without an amine.

Table 5-2. Atomic coordinates and B_{eq} for the copper-vanillin-water complex.

Atom	x	y	z	B_{eq}
Cu1	0.00000	0.16855(2)	1/4	1.338(8)
O1	0.04237(6)	0.18630(10)	0.4990(2)	1.79(2)
O2	0.07338(7)	0.31660(10)	0.2457(2)	2.27(3)
O3	0.31713(6)	0.4099(2)	0.8076(2)	3.35(3)
O4	-0.06135(7)	0.03210(10)	0.3012(2)	2.57(3)
C1	0.09710(7)	0.24490(10)	0.5414(2)	1.56(3)
C2	0.11715(8)	0.31550(10)	0.4095(2)	1.52(3)
C3	0.17512(8)	0.3736(2)	0.4479(2)	1.86(3)
C4	0.21534(8)	0.3642(2)	0.6223(2)	1.91(3)
C5	0.19501(8)	0.2988(2)	0.7541(2)	2.15(3)
C6	0.13712(8)	0.2399(2)	0.7148(2)	2.02(3)
C7	0.27834(8)	0.4168(2)	0.6612(3)	2.16(4)
C8	0.08880(10)	0.3802(3)	0.1003(3)	4.10(5)
H1	0.18830	0.42090	0.35430	2.1778
H2	0.22250	0.29460	0.87640	2.5835
H3	0.12400	0.19400	0.80990	2.3928
H4	0.29090	0.46090	0.56410	3.0416
H5	0.09690	0.47030	0.13230	4.6721
H6	0.12660	0.34300	0.07740	4.6721
H7	0.05370	0.37410	-0.00720	4.6721
H8	-0.0500(10)	-0.020(2)	0.356(3)	2.7(5)
H9	-0.0930(10)	0.046(2)	0.307(3)	2.5(5)

Table 5-3. Selected bond length (Å) for the copper-vanillin-water complex.

Atom	Atom	Distance	Atom	Atom	Distance
Cu1	O1	1.911(1)	Cu1	O1*	1.911(1)
Cu1	O2	2.255(1)	Cu1	O2*	2.255(1)
Cu1	O4	2.082(1)	Cu1	O4*	2.082(1)
O1	C1	1.317(2)	O2	C2	1.373(2)
O2	C8	1.420(2)	O3	C7	1.226(2)
C1	C2	1.419(2)	C1	C6	1.396(2)
C2	C3	1.376(2)	C3	C4	1.407(2)
C4	C5	1.394(3)	C4	C7	1.450(2)
C5	C6	1.379(2)			

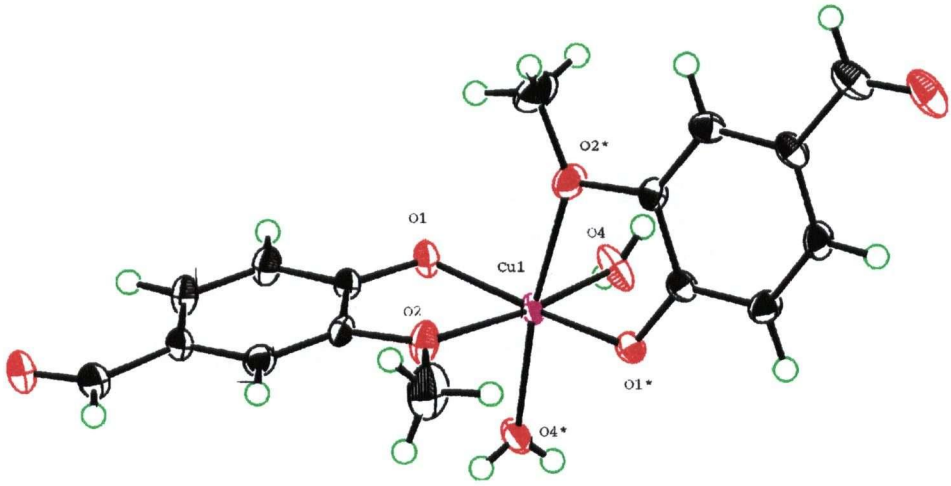


Figure 5-2. Perspective view of bis(vanillinato)di(H_2O)Cu(II) with the atomic numbering.

Table 5-4. Selected bond angle (°) for the copper-vanillin-water complex.

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
O1	Cu1	O2	77.39(5)	O2	C2	C1	112.78(14)
O1	Cu1	O4	92.85(6)	O2	C2	C3	125.65(14)
O1	Cu1	O1*	168.72(5)	C1	C2	C3	121.57(14)
O1	Cu1	O2*	94.69(5)	C2	C3	C4	119.44(16)
O1	Cu1	O4*	94.97(6)	C5	C4	C7	120.64(16)
O2	Cu1	O4	170.24(6)	C3	C4	C5	119.25(17)
O1*	Cu1	O2	94.69(5)	C3	C4	C7	120.03(17)
O2	Cu1	O2*	92.01(5)	C4	C5	C6	121.12(15)
O2	Cu1	O4*	88.72(5)	C1	C6	C5	120.66(15)
O1*	Cu1	O4	94.97(6)	O3	C7	C4	124.50(19)
O2*	Cu1	O4	88.72(5)	C2	C3	H1	120.25
O4	Cu1	O4*	92.20(5)	C4	C3	H1	120.31
O1*	Cu1	O2*	77.39(5)	C4	C5	H2	119.19
O1*	Cu1	O4*	92.85(6)	C6	C5	H2	119.69
O2*	Cu1	O4*	170.24(6)	C1	C6	H3	119.80
Cu1	O1	C1	118.12(11)	C5	C6	H3	119.54
Cu1	O2	C2	108.33(9)	O3	C7	H4	117.57
Cu1	O2	C8	131.19(13)	C4	C7	H4	117.93
C2	O2	C8	118.27(16)	O2	C8	H5	108.95
H8	O4	H9	109(3)	O2	C8	H6	109.86
Cu1	O4	H9	123.5(17)	O2	C8	H7	109.79
Cu1	O4	H8	120.9(19)	H5	C8	H6	109.07
C2	C1	C6	117.90(14)	H5	C8	H7	109.05
O1	C1	C6	121.86(14)	H6	C8	H7	110.08
O1	C1	C2	120.24(14)				

Table 5-5. Hydrogen bonds (Å) and C-H….O interactions.

A	H	B	A-H	H….B	A….B	A-H….B(°)
O4	H8	O1	0.70(3)	2.06(3)	2.946(2)	165(3)
O4	H9	O3	0.73	2.02	2.755(2)	176.4
C4	H8	O4	0.70(3)	3.11(2)	3.000(3)	128(2)

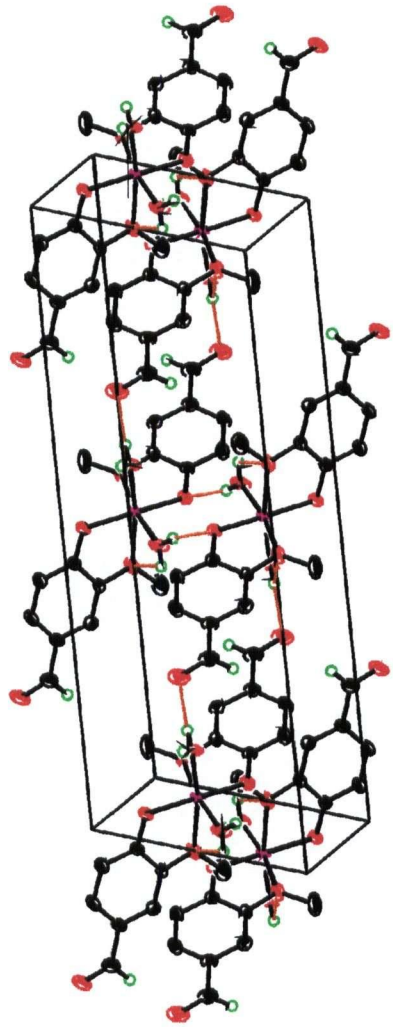


Figure 5-3. The packing of bis(vanillinato)di(H_2O)copper(II) monoclinic unit cell.

5.3.2.2 The spectroscopic examination

FTIR spectra

The FTIR spectra of the crystalline red solid and pure vanillin are shown in Figure 5-4. The peak at 3182 cm^{-1} in the spectrum of pure vanillin was assigned to the -OH stretching vibration. However, in the spectrum of the red complex, two peaks were observed at 3262 cm^{-1} and 3368 cm^{-1}. They are assigned to the intra-molecular and inter-molecular hydrogen bonded water in the complex. The carbonyl stretching vibration is observed at 1668 cm^{-1} in vanillin but is shifted to the lower frequency of 1650 cm^{-1} in the copper complex due to the hydrogen bonding. The peak at 734 cm^{-1} in the spectrum of

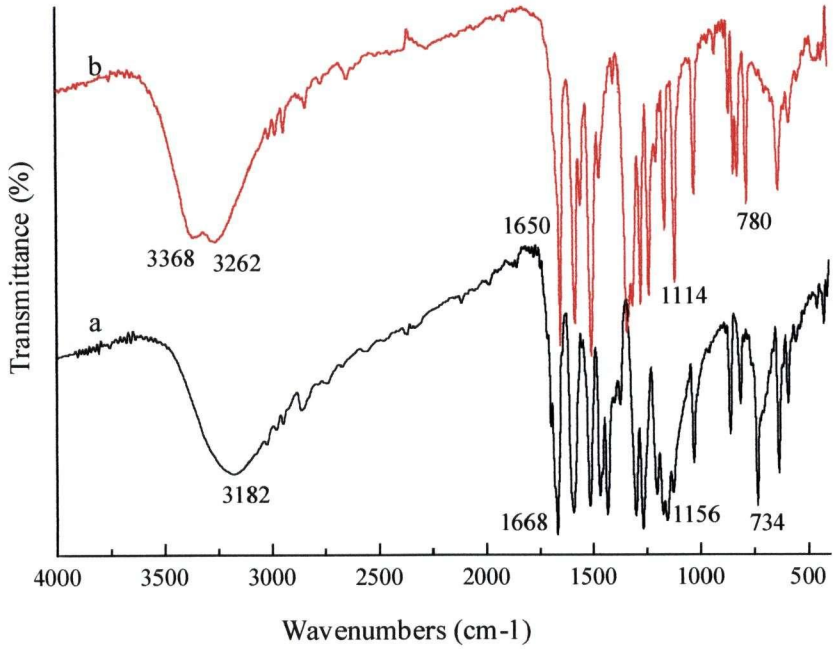


Figure 5-4. FTIR spectra of a) vanillin, and b) vanillin-copper complex.

vanillin, attributed to the phenolic OH out of plane deformation, was absent in the spectrum of the red solid. This observation confirmed the conclusion that the phenolic hydroxyl group was involved in the formation of the copper complex. The peak at 1156 cm^{-1}, due to C-O-C bonding in pure vanillin, was relocated to 1114 cm^{-1} in the complex similar to that observed for the di(ammine)bis(vanillato)copper(II) complex (Xie et al., 1995). The shift to lower frequency is consistent with the methoxyl group in vanillin taking part in the formation of the complex.

ESR spectroscopy

The ESR spectrum of the red complex, dissolved in DMSO, was obtained at low temperature of 150 K, and is shown in Figure 5-5. The hyperfine splitting is exhibited at the lower field with $g_{//} = 2.37$, and $A_{//} = 132$, associated with the unresolved absorption at higher field ($g_{\perp} = 2.07$). Thus the bis(vanillato)copper(II)dihydrate complex showed a much smaller $A_{//}$ and a larger $g_{//}$ value than the vanillin-copper-ammonia complex ($A_{//} = 175$, $g_{//} = 2.295$), which contains two nitrogen atoms (Xie et. al., 1995). This reduction in $A_{//}$ and increase in $g_{//}$ in the ESR parameters of the red complex reflects the orthorhombic system in which all bonding to the central copper is formed by oxygen. The ESR g and A values for the red bis(vanillato)copper(II)dihydrate are in good agreement with those recorded for copper sulphate in water ($g_{//} = 2.40$, $A_{//} = 138$, and $g_{\perp} = 2.07$) (Xie et al., 1995), as well as copper sulphate treated wood ($g_{//} = 2.372$, $A_{//} = 132$, and $g_{\perp} = 2.082$) (Ruddick, 1992b). This is consistent with the copper in the red complex being present as a square planar or octahedral molecule in which planar bonding of copper to four oxygen

atoms is present. This structure is confirmed by that determined using X-ray crystallography.

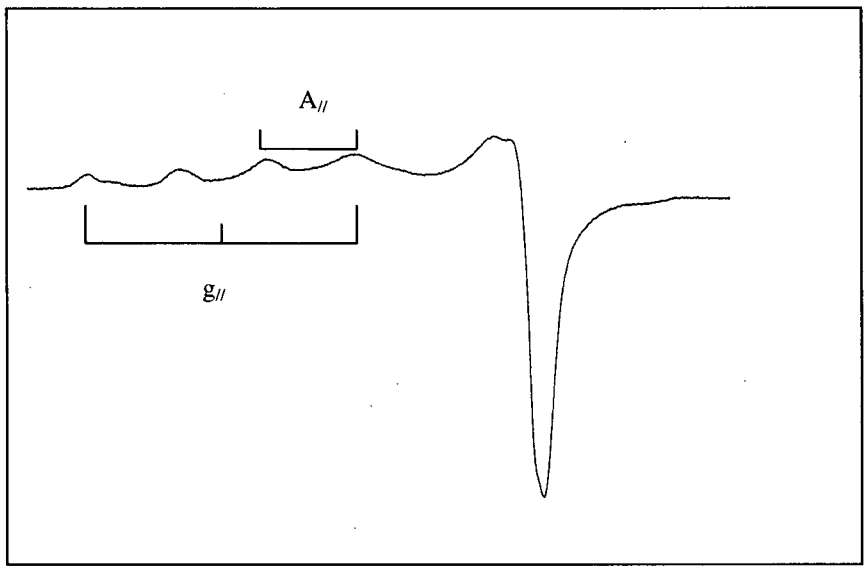


Figure 5-5. ESR spectrum of vanillin-copper complex in DMSO solution at 150K.

5.4. Conclusions

The FTIR spectra verified that the reaction product, formed between copper-HDO monoethanolamine and vanillin, is copper$(HDO)_2$. This suggested that the reactions involving the HDO ligand may be dominated by precipitation rather than the formation of copper amine wood complexes.

A red, water insoluble copper-vanillin-water complex, formed by reacting a solution of copper in ethylenediamine with vanillin, a lignin model compound, was characterized by X-ray crystallography, FTIR and ESR. The x-ray crystal structure confirmed that the red $Cu(vanillin)_2(H_2O)_2$ complex was octahedral. The central copper was bonded to two oxygen atoms from the methoxyl groups in vanillin, and two oxygen atoms from water, in a planar arrangement. The water molecules are arranged cis to each other. This very distorted octahedral configuration is completed by two Cu-O (phenolic) bonds with $Cu\text{-}O_{axial} < Cu\text{-}O_{in\text{-}plane}$. The x-ray structure confirmed the chemical analysis which revealed that no ethylenediamine was retained during complex formation. It is suggested that a similar reaction between ethylenediamine copper solution and lignin in wood will take place to form a stable lignin-copper complex without nitrogen present.

Chapter 6

Reactions of organosolv lignin with copper-amine and copper-HDO amine solutions

6.1. Introduction

Lignin is a complex, high molecular weight polymer, built of phenylpropane units. The presence of many different carbon-to-carbon linkages between the units makes it difficult to degrade the polymer to low-molecule-weight fragments. It has not yet been possible to isolate all parts of the lignin completely from wood without engendering structural changes (Hon and Shiraishi, 1991). The major functional groups in lignin are: methoxyl, phenolic hydroxyl, and some terminal aldehyde groups in the side chain. Table 6-1 gives a rough idea of relative occurrence of functional groups in lignin (Sjostrom, 1989).

Table 6-1. Functional groups of lignin (per 100 C_6C_3 units)

Group	Softwood lignin	Hardwood lignin
Methoxyl	92-97	139-158
Phenolic hydroxyl	15-30	10-15
Benzyl alcohol	30-40	40-50
Carbonyl	10-15	--

Several studies of the fixation of ammoniacal copper systems in wood have demonstrated that lignin is the dominant fixation site for copper. One of the reaction

pathways proposed by Butcher and Wilson (1982), and Jin and Preston (1991) is that copper in ammoniacal copper solutions reacts with the acidic functional groups, such as phenolic hydroxyl group of lignin, by ion exchange. Such a reaction may take place with the formation of simple copper compounds. Alternatively, diamminecopper complexes may be formed (Xie et. al., 1995). Lebow and Morrell (1995) used high-quality organosolv spruce lignin to investigate copper adsorption. They observed that, compared to other wood components, lignin adsorbed the largest amount of copper when reacted with an ACZA solution. This is consistent with the studies by Doyle (1995) who investigated the ion exchange of quaternary ammonium compounds with protons on cellulose and lignin. The high affinity of copper for lignin suggested that under alkaline conditions phenolic groups are primary reaction sites. This was verified by the disappearance of phenolic hydroxyl signal in the FTIR spectra (Lebow and Morrell, 1995; Liu et. al., 1994; Zhang and Kamdem, 2000).

Dagarin *et. al.* (1996) employed ESR spectroscopy to examine the time dependence of interactions between ammoniacal copper and brown rotted lignin, cellulose and wood meal. Immediately after treatment, the ESR spectrum of copper in brown rotted lignin was completely different from that of the ammoniacal copper solution, indicating the rapid formation of a copper complex with lignin. The time dependence studies of interaction between wood components and ammoniacal copper in the research by Dagarin *et. al.* strongly supported the hypothesis that the fastest and most significant reactions are those between ammoniacal copper and lignin.

Softwood organosolv lignin was used in this study. The objective of this part of experiment is to investigate the reactions of organosolv lignin and copper-amine and copper-HDO amine solutions. The major products formed during the reactions will be identified by using FTIR, ESR and XPS. The knowledge from the fixation reaction between organosolv lignin and copper-amine or copper-HDO amine solutions will assist the interpretation of similar reactions, which may take place in wood.

6.2. Materials and methods

6.2.1. Sample treatment

Softwood organosolv lignin was purchased from Aldrich Co. About 2.0 g organosolv lignin was treated with 50 g of 1.0% (expressed as CuO) copper-amine and copper-HDO amine solutions in a 100 ml beaker. The beaker was then sealed and the solution stirred on VarioMag® shaker overnight, using a magnetic bar. After the stirring, the treated organosolv lignin was filtrated through a glass fiber mat and washed with deionized water until the conductivity of the eluent water was constant. The conductivity was monitored by a volt (mV) meter. The objective of continuous washing with water was to remove unreacted amine, HDO or copper, and minimize physical adsorption of copper in the treated samples. The treated and water-washed samples were air-dried for two weeks.

6.2.2. Sample analysis

FTIR analysis was performed on a Perkin-Elmer 1600™ spectrophotometer. Air-dried samples were mixed with KBr before the spectra were collected. FTIR spectrum was acquired for a total of 4 scans over 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. Compressed pellets were prepared for XPS analysis. A Leybold Max200™ spectrometer was used for XPS measurements. The XPS operating parameters were the same as those described in Section 4.2.3.

The treated organosolv lignin was added to an ESR quartz tube until it was filled to about 4 mm in height. A Brucker ECS 106™ spectrometer was used to record the spectra of the treated organosolv lignin samples. All measurements were made at room temperature. Other ESR operating parameters applied have been previously described in Table 4-2.

6.3. Results and discussion

6.3.1. FTIR Spectra

FTIR spectrum of organosolv lignin is shown in Figure 6-1. The assignment of the band at 1700 cm^{-1} in lignin is difficult since unconjugated ketones, conjugated carboxylic acids and their correspondent esters absorb in this region (Hergert, 1971; Sarkanen et al. 1967). It has been reported that ketones in lignin have a characteristic carbonyl stretching vibation at 1700-1715 cm^{-1}. The lignin model compounds, guaiacyl acetone, β-hydroxylconiferyl alcohol and 1-ethoxyl-1-guaiacyl-2-propanone, show absorption bands at 1705, 1709, and 1710 cm^{-1} respectively (Hergert, 1971). This

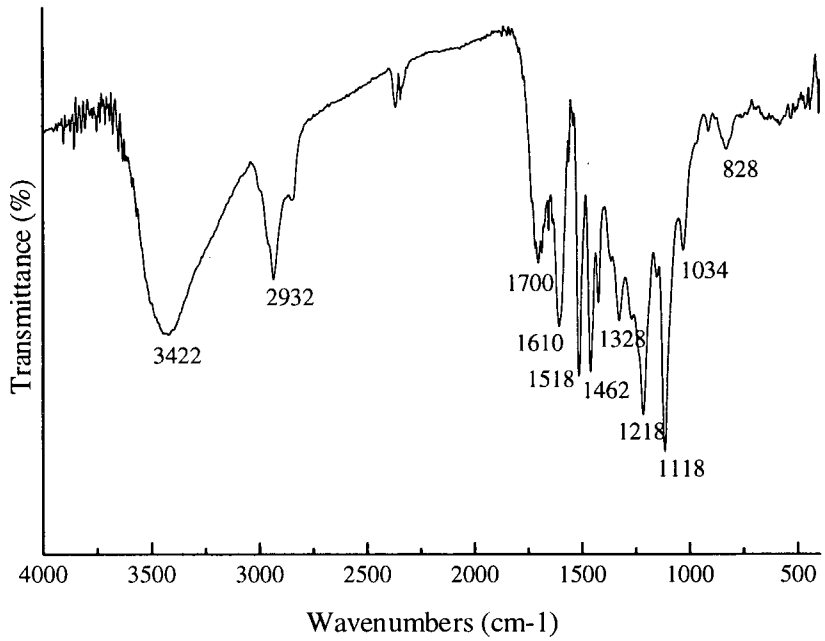


Figure 6-1. FTIR spectrum of organosolv lignin

suggests that the 1700 cm^{-1} band may be due to carbonyl vibration in unconjugated ketone groups. However, Smith (1995) and Sarkanen et. al. (1967) pointed out that this band was attributed to the carbonyl stretching vibration in esters of acids, such as p-hydroxybenzoic, vanillin, p-hydroxycinnamic and ferulic acids. Sarkanen et. al. (1967) also observed that treatment of ponderosa pine lignin with a buffer solution of pH 7 did not change this band, indicating that this band is not from carboxylic acid groups.

Figures 6-2 to 6-4 show the FTIR spectra of amine treated and Cu-amine treated lignin. The peak at 1700 cm^{-1} was diminished for both treatments. The pH of the amine and copper-amine solutions is above 10. With such an alkaline solution, the ester groups with an absorption at 1700 cm^{-1} can be hydrolyzed to produce aromatic carboxylic acid groups (Sarkanen et. al., 1967). On the other hand, the ketone carbonyl (giving rise to the absorption band at around 1700 cm^{-1}) in lignin can also form carboxylic groups through oxidation. For amine treatment, the reduction in peak of 1700 cm^{-1} suggests the formation of amine-acid salt, which results in the slight increase of the peak at 1610 cm^{-1}, related to C=O stretching in carboxylate and N-H bending in amine acid salts. For copper-amine treatment, the aromatic carboxylic acid groups, created by hydrolyzing and oxidizing, can further interact with copper, leading to the formation of copper-carboxylate salts. This accounts for the disappearance of peak at 1700 cm^{-1} and the slight increase of the peak intensity at 1610 cm^{-1}.

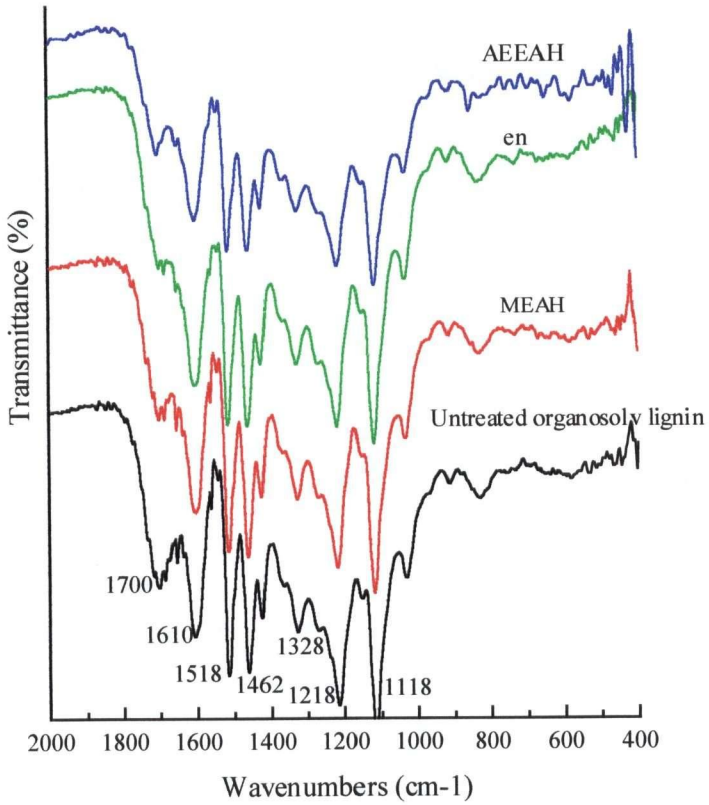


Figure 6-2. FTIR spectra of untreated and amine treated organosolv lignin.

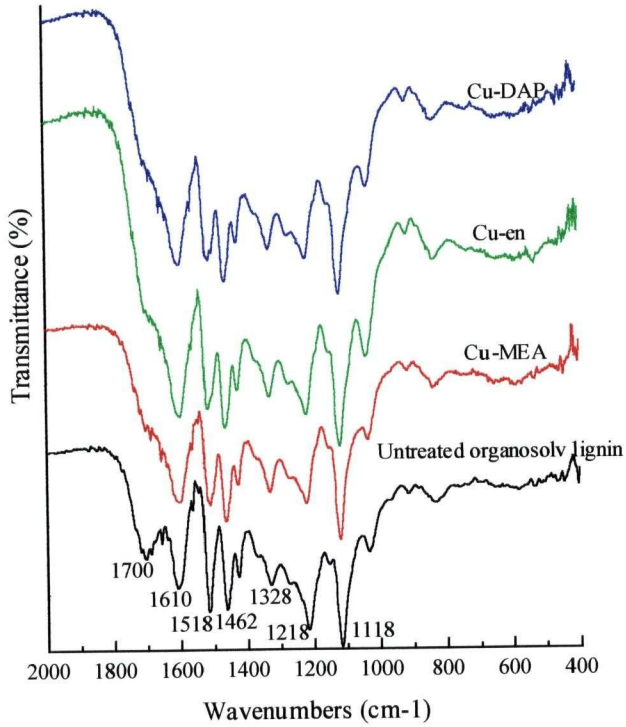


Figure 6-3. FTIR spectra of untreated and copper-amine treated organosolv lignin.

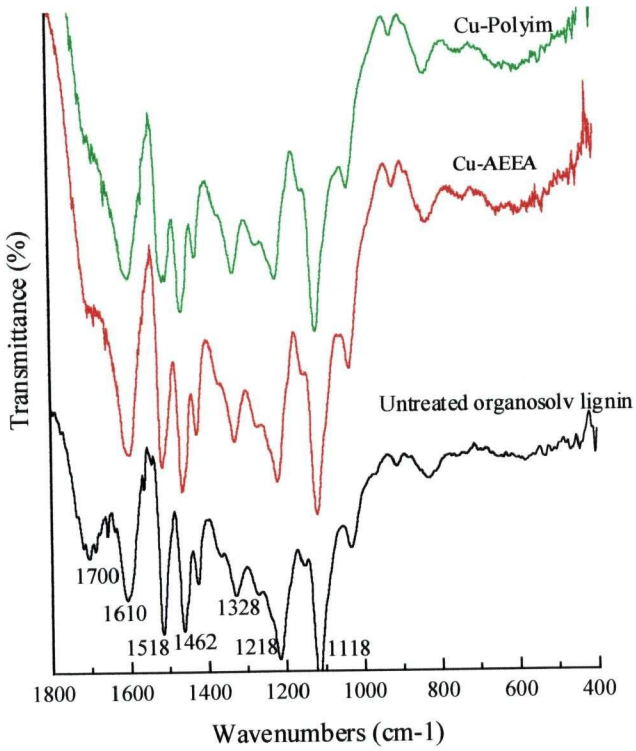


Figure 6-4. FTIR spectra of untreated and copper-amine treated organosolv lignin.

The absorption band at 1518 cm^{-1} and 1462 cm^{-1} in lignin are assigned to aromatic skeletal vibration (Michell et. al., 1965; Hergert, 1971). The absorption at 1518 cm^{-1} is a characteristic peak of lignin due to the C=C stretching vibration of the aromatic ring present in lignin. The decrease in intensity of this peak in amine treated and copper-amine treated samples implies that the substituents of the aromatic rings have been changed by the chemical bonding of the treating solutions. This is also indicated by a slight increase in the peak intensity at 1462 cm^{-1} in the treated samples. The absorption at 1462 cm^{-1} is assigned to an aromatic skeletal vibration, a ring stretching mode coupled with C-H deformation, which is sensitive to the nature of ring substitutes (Hergert, 1971). These changes can be interpreted that amine and copper-amine treatment could alter the aromatic ring substituents by, for instance, the hydrolysis of aromatic esters and/or oxidative cleavage of ketone carbonyl groups. However, copper amine treatment showed a greater change in these two peaks compared to amine treatment, indicating a greater degree of the hydrolysis and/or cleavage reactions.

The absorption at 1218 cm^{-1} in lignin has been assigned to phenolic O-H deformation (Kolboe and Ellefsen, 1962; Sarkanen et. al., 1967; Hergert, 1971), although C-H deformation also absorbs in this region (Sarkanen et. al., 1967). Amine treatment does not cause a significant change in the peak of 1218 cm^{-1}, suggesting the reaction between amine and phenolic hydroxyl groups is not dominant. However, for the copper-amine treatment, the peak of 1218 cm^{-1} is noticeably reduced. This is due to the reaction of the phenolic hydroxyl groups forming stable copper phenolate complexes with copper. The decrease in intensity of the peak of 1218 cm^{-1} tends to be larger for Cu-MEA and

Cu-Polyim treated samples than for the copper-diamine (Cu-en, Cu-DAP, and Cu-AEEA) treated samples (Figure 6-3, 6-4). This suggests a higher ability to form copper-lignin complexes for copper-monoethanolamine than for copper-diamine solution. This observation is consistent with the leaching performance of the copper amine treated samples, in which the copper-monoethanolamine treated wood was more leach resistant than the copper-diamine treated wood (Chapter 3).

FTIR spectra of copper-HDO amine treated organosolv lignin are presented in Figures 6-5 and 6-6. The FTIR spectra of copper-amine treatment and copper-HDO amine treatment are very similar. The most important changes take place on the peaks of 1700, 1610, 1518, 1462, and 1218 cm^{-1}. The reduction of the peak at 1700 cm^{-1} and the enhancement of peak at 1610 cm^{-1} suggest the formation of copper-carboxylates with lignin. The relative intensity of 1518 cm^{-1} ring stretching band and 1462 cm^{-1}, due to C-H bonds, is reversed. This is contributed by the hydrolysis of aromatic esters and/or oxidative cleavage of ketone carbonyl groups. The intensity of the peak at 1218 cm^{-1} decreased after copper-HDO amine treatment. The reduction was particularly noticeable for the copper-HDO DAP treated samples. This confirms the conclusion reached in the leaching experiment again, where the copper-HDO DAP showed the best leaching resistance (Chapter 3).

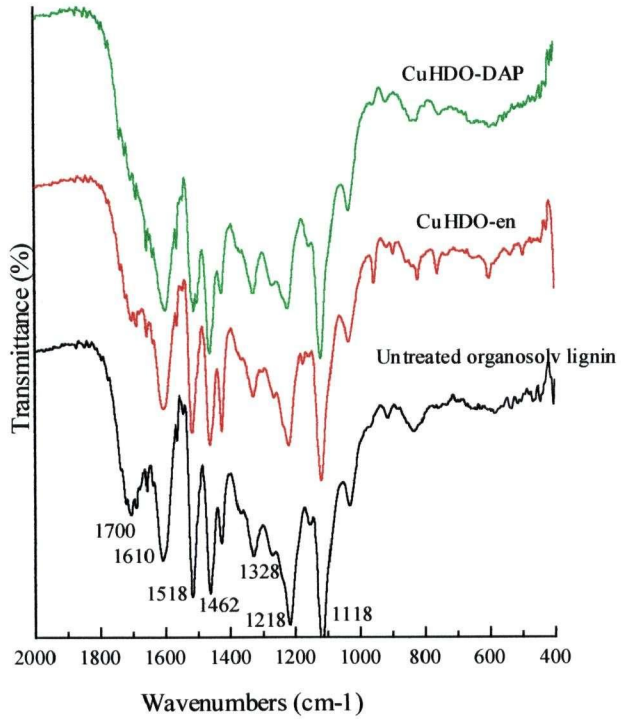


Figure 6-5. FTIR spectra of untreated and copper-HDO amine treated organosolv lignin.

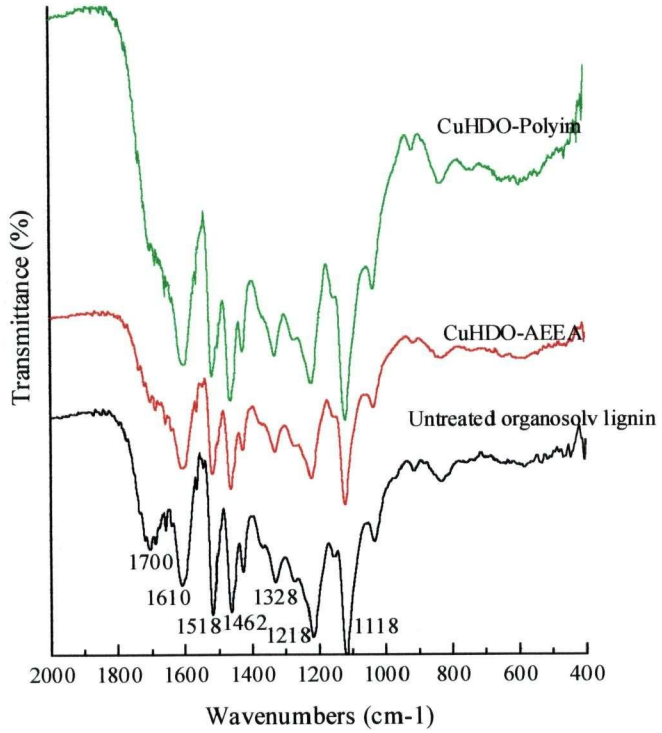


Figure 6-6. FTIR spectra of untreated and copper-HDO amine treated organosolv lignin.

6.3.2. XPS spectra

The C1s spectrum of untreated organosolv lignin was fitted into three peaks (Figure 6-7), in which the C1 type carbon (C-C or C-H type) was dominant. This is expected since lignin primarily contains phenyl propane aromatic ring structural units. The C2 type carbon, corresponding to C-O bonding, was the second largest peak, which arose from ether linkages such as α-O-4 and β-O-4 linkage. The smallest peak was due to C3 type carbon, associated with the O-C-O linkage or carbonyl group (C=O). After the treatment with either amine, copper-amine, or copper-HDO amine solution, C2 did not show any significant change, but the C3 peak increased for all the cases (Figure 6-7). It has been established that certain C-O-C bonds would be cleaved by alkaline hydrolysis reactions of organosolv lignin to produce C3 or C4 type of carbons (Thring, et. al., 1989). Accordingly, C3 is seen to increase. However, the lack of change in C2 can be attributed to the presence of amine in which the carbon is primarily C2 type of carbons containing C-N and C-O bonding.

The N1s spectra of amine treated organosolv lignin show a single peak with the binding energy located between 400.43 to 401.2 eV (Table 6-2). This is consistent with the reported binding energy for amine acid salts of 400.3 to 401.0 eV (Nordberg et. al., 1967). It was found that ester groups in lignin could be hydrolyzed into an aromatic carboxylic acid under the highly basic conditions during treatment (Sarkanen et. al., 1967). Carboxylic acid produced can further react with amine to form an amine acid

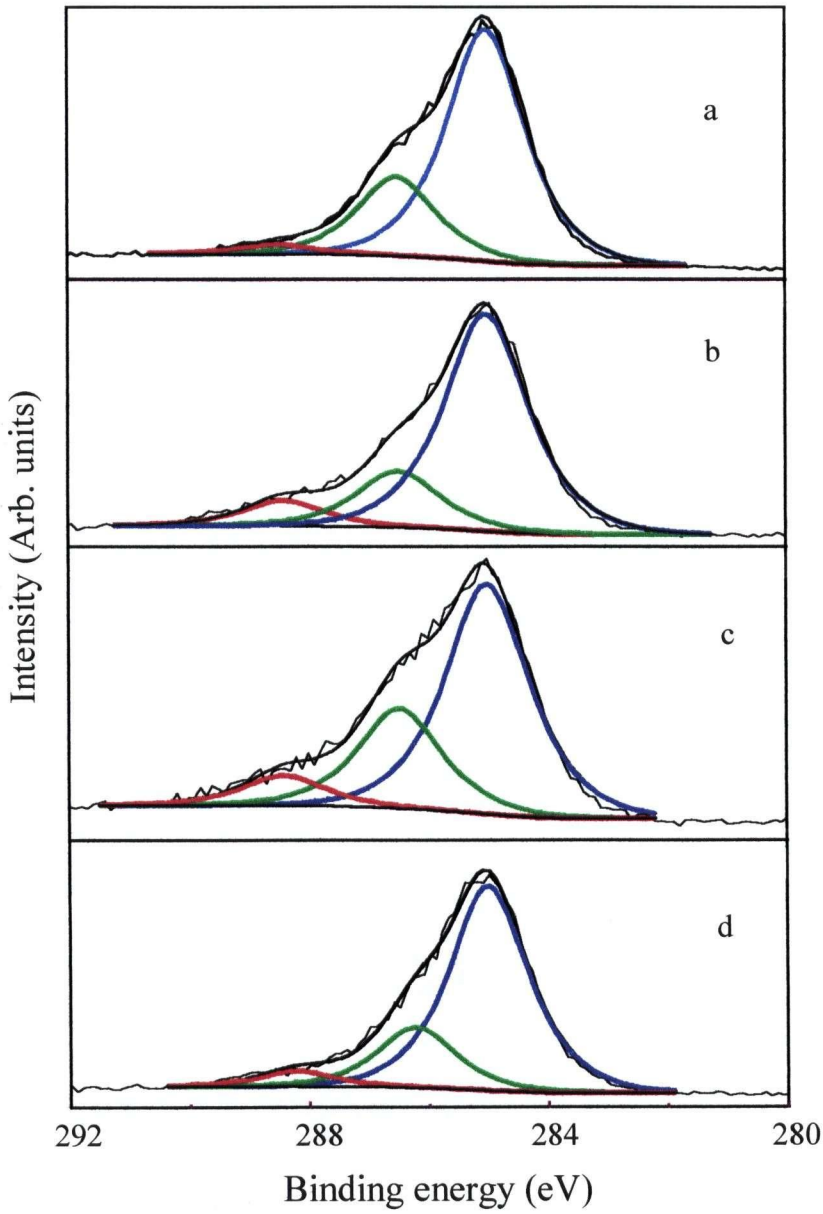


Figure 6-7. XPS C1s spectra of a) organosolv lignin, b) en treated organosolv lignin, c) Cu-en treated organosolv lignin, and d) CuHDO-en treated organosolv lignin.

salt. Since all treated samples were completely washed, the presence of this peak suggested that the amine-acid salt formed was resistant to water leaching, confirming the FTIR observations.

Table 6-2. The binding energies of C1s and N1s spectra for untreated and amine treated samples.

Sample ID	C1s (eV)			N1s (eV)
	C1	C2	C3	
Organosolv-lignin	285.00	286.49	288.52	
MEAH treated	285.00	286.50	288.34	401.18
en treated	285.00	286.48	288.40	400.43
AEEAH treated	285.00	286.56	288.42	400.54

The N1s spectra of copper-amine treated organosolv lignin showed two well resolved nitrogen peaks, labelled as N1 and N2 (Table 6-3). For copper monoethanolamine treated samples (Cu-MEA and Cu-Polyim treatments), the smaller peak is located at ca. 399.3 eV of the binding energy, while the larger peak is at ca. 400.3 eV (Figure 6-8). The binding energy at ca. 399.3 eV, related to the formation of copper-amine complex with lignin (Section 4.3.2), is significantly higher than that for free amine (398.9 eV). The increase in the nitrogen binding energy is caused by the lower electron density on the nitrogen due to the donation of electrons onto the copper. The higher energy peak is in agreement with the reported binding energy for an amine acid salt.

Table 6-3. The binding energies of C1s, N1s and Cu2p for copper-amine and copper-HDO amine treated samples.

Sample ID	C1s (eV)			N1s (eV)			Cu2p (eV)	
	C1	C2	C3	N1	N2	N3	Cu1	Cu2
Cu-MEA	285.00	286.49	288.68	399.26 (521)*	400.48 (1268)		933.11	934.85
Cu-Polyim	285.00	286.37	288.18	399.51 (928)	400.29 (2181)		932.94	934.80
Cu-en	285.00	286.47	288.41	399.96 (2323)	401.35 (782)			934.55
Cu-DAP	285.00	286.49	288.40	399.74 (1345)	400.51 (749)		933.12	934.81
Cu-AEEA	285.00	286.31	287.97	399.74 (1050)	400.70 (734)		933.01	934.57
CuHDO-en	285.00	286.22	288.22	400.22 (623)		402.76 (2388)	933.12	934.69
CuHDO-DAP	285.00	286.36	288.35	399.88 (1835)	400.64 (489)	402.63 (651)	933.27	934.86
CuHDO-AEEA	285.00	286.41	287.94	399.99 (943)	400.66 (416)	402.52 (142)		934.49
CuHDO-Polyim	285.00	286.56	288.71	399.66 (1628)	400.50 (1092)	401.71 (564)		934.41

* N1s peak area.

Since both Cu-MEA and Cu-Polyim contain the high mole ratio of amine to copper (4:1) in the formulations, the excess amine is able to further react with the organoslov lignin to produce an amine-acid salt. Unlike the copper monoethanolamine treatment, the major peak for the copper diamine treated organosolv lignin appears at 399.8 eV, associated with the binding energy of nitrogen in the copper-amine complexes. The minor peak, located at 400.5 eV, is due to the formation of an amine-acid salt with the hydrolyzed carboxylic acid group in lignin during fixation (Table 6-3, Figure 6-8).

In the Cu2p spectra for the samples, treated with copper amine solutions, the smaller peak, located at the lower binding energy of ca. 933.2 eV (Table 6-3), resulted from the reduction of copper(II) during XPS analysis (Section 4.3.2.1). For all copper-amine treated organosolv lignin, the presence of copper(II) compounds during fixation is confirmed by the presence of the shake-up satellite peak(s) (Figure 6-9). The major peak of Cu2p has the binding energy of ca. 934.7 eV. This binding energy compares well with the previous assignment of the copper binding energy in di(amine)bis(vanillinato) copper(II) complex (934.62 eV), implying that a similar copper complex is formed with organosolv lignin. The electron density on the copper atom is directly correlated to its binding energy. It was suggested that the electron donor capacity and the type of bond (i.e. donor bond or σ bond) of the ligand forms with copper influences the electron density on the copper atom, and thus affects its binding energy (Frost et. al., 1972).

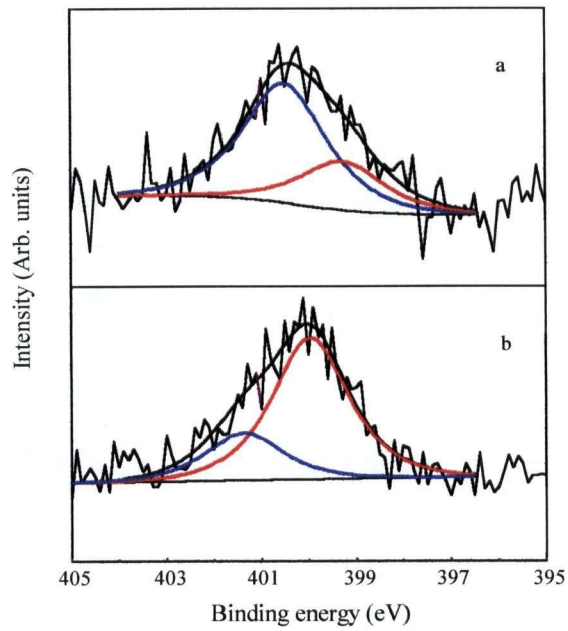


Figure 6-8. XPS N1s spectra of a) Cu-MEA treated organosolv lignin, and b) Cu-en treated organosolv lignin.

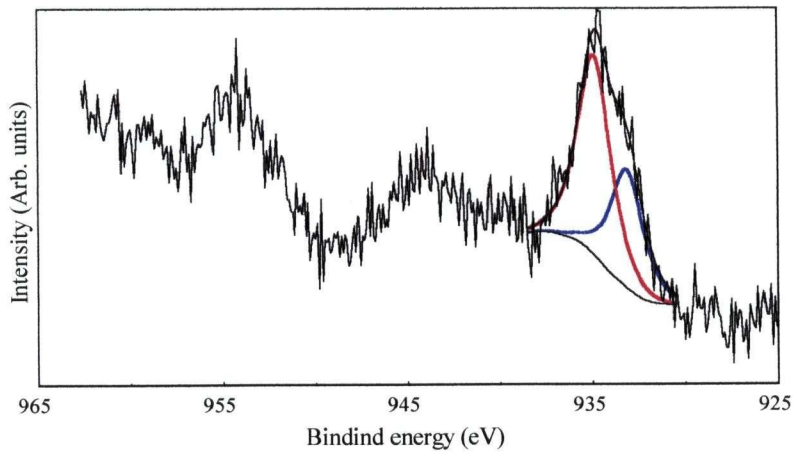


Figure 6-9. XPS Cu2p spectrum of Cu-MEA treated organosolv lignin.

For copper-HDO amine treatment, the N1s spectra displayed a different pattern from those of the copper amine treatments. CuHDO-en treated sample shows two well resolved nitrogen peaks, located at 400.22 eV and 402.76 eV, respectively (Table 6-3 and Figure 6-10). The predominant peak with the average binding energy of 402.76 eV (but which is actually comprised of two peaks at ca. 402.0 and 402.9 eV) arises from the binding energy of nitrogen in the $Cu(HDO)_2$ precipitate, confirming that the precipitation reaction of $Cu(HDO)_2$ is one of the dominant reactions during fixation. The smaller peak at 400.22 eV is consistent with the binding energy assigned to the nitrogen in copper amine wood complex. The residual copper after precipitation can react with the phenolic hydroxyl groups in lignin to form a copper-amine-lignin complex. For CuHDO-DAP, CuHDO-AEEA and CuHDO-Polyim treatment, the N1s spectra were best fitted into three peaks, located at ca.399.9 eV, 400.7 eV, and 402.5 eV, respectively (Table 6-3, Figure 10). For these three treatments, the binding energy at 399.9 eV is the largest peak, associated with the formation of a copper-amine-lignin complex. The second largest peak appears at ca. 400.7 eV, consistent with the assigned nitrogen binding energy for the amine-acid salt. The reaction of organosolv lignin and the excess amine or released free amine after the formation of the copper-amine-lignin complex, could account for the formation of the amine-acid salt. The smallest peak is located at ca. 402.5 eV, which is the characteristic peak for $Cu(HDO)_2$ precipitate, confirming the presence of $Cu(HDO)_2$ precipitate after treatment. However, the small peak area implies the precipitation reaction of $Cu(HDO)_2$ in these treatments is less important during fixation. For the Cu2p spectra, the lower binding energy is due to the reduction of Cu(II) to Cu(I) during

exposure to x-ray in XPS analysis. The major peak with the higher binding energy is corresponding to the binding energy of copper in the copper-amine-lignin complex. Because of the presence of a copper(I) compound and the anticipated small influence of the copper from $Cu(HDO)_2$, it was not possible to fit this copper spectrum to include a compound due to $Cu(HDO)_2$.

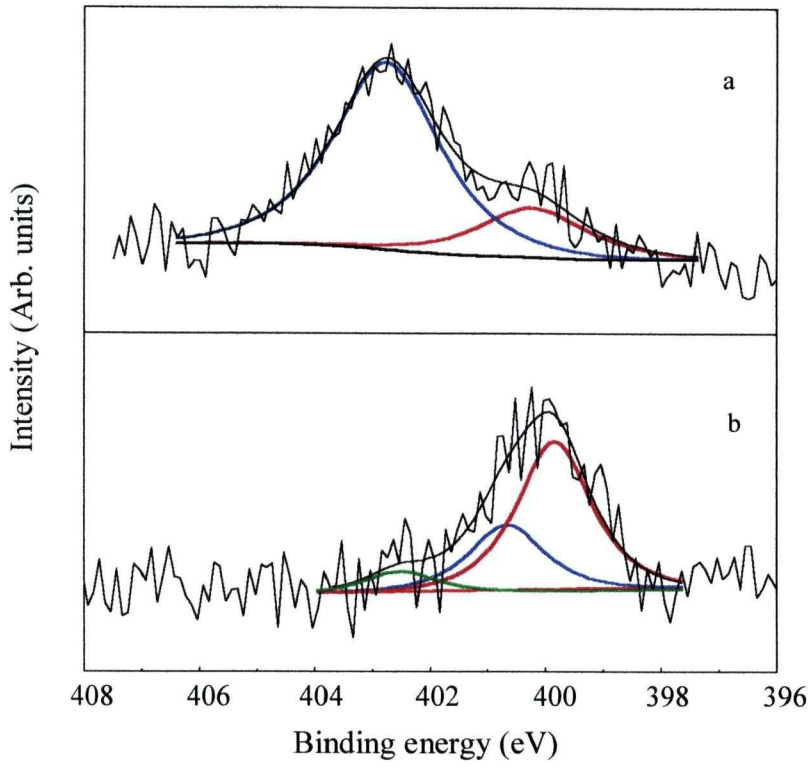


Figure 6-10. XPS N1s spectra of a) CuHDO-en treated organosolv lignin, and b) CuHDO-AEEA treated organosolv lignin.

6.3.3. ESR spectra

Representative ESR spectra of copper amine and copper-HDO amine treated organosolv lignin are shown in Figure 6-11. For all samples, only one copper species could be detected based on the $g_{//}$ region of the spectra. The ESR spectral parameters are presented in Table 6-4.

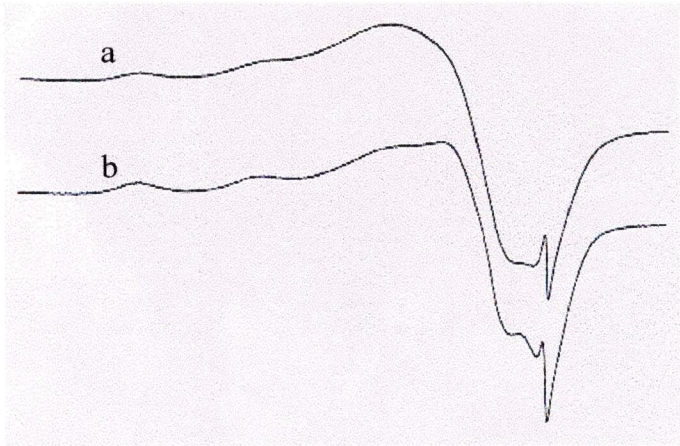


Figure 6-11. ESR spectra of a) Cu-DAP treated organosolv lignin, and b) CuHDO-AEEA treated organosolv lignin.

Table 6-4. ESR spectral parameters of $g_{//}$ and $A_{//}$ for copper-amine and copper-HDO amine treated organosolv lignin.

Sample ID	$g_{//}$	$A_{//}$
Cu-MEA	2.269	170
Cu-Polyim	2.264	165
Cu-en	2.211	195
Cu-DAP	2.217	193
Cu-AEEA	2.222	189
CuHDO-en	2.226	188
CuHDO-DAP	2.221	190
CuHDO-AEEA	2.220	188
CuHDO-Polyim	2.229	189

The copper monoamine treated samples (Cu-MEA and Cu-Polyim treatment) have similar $g_{//}$ and $A_{//}$, and can be grouped together. Comparing their values of $g_{//}$ and $A_{//}$ with those reported (Table 4-7), it is suggested that the structure of the copper complex formed in copper monoamine treated lignin, is copper bound to two nitrogen atoms from amines and two oxygen atoms from the lignin. This observation is consistent with the results from the corresponding copper-amine treated wood. The copper-diamine treated organosolv lignin shows much lower $g_{//}$ value, but higher $A_{//}$ value. The $g_{//}$ and $A_{//}$ agree well with copper species bound to four nitrogen atoms in a plane. In general, the copper complexes formed in organosolv lignin are similar to those formed in wood, providing support that lignin plays an important role in the fixation of copper in wood.

The values of $g_{//}$ and $A_{//}$ recorded for copper-HDO amine treated organosolv lignin are consistent with those for treated wood, and we tentatively assigned them to $Cu(HDO)_2$ precipitate. However, a second copper species identified by XPS analysis, is not obvious in the ESR spectra. The cause of this phenomenon is not clear, but may be due to a surface coating of a second copper species. An alternative explanation is the extremely high concentration of the copper species, which would result in weak broad lines in the ESR spectrum. The copper species observed in the ESR spectrum of CuHDO-en treatment is assigned to copper bound to four nitrogen atoms in the copper-amine-lignin complex (Figure 6-10).

6.4. Conclusions

Lignin plays a significant role in the fixation of copper or amine in copper-amine and copper-HDO amine treatments of wood as identified by FTIR, XPS and ESR. FTIR spectra. Amine, copper-amine and copper-HDO amine treatments of organosolv lignin confirmed that the phenolic hydroxyl and ester groups in the lignin are the major bonding sites for copper and amine.

FTIR and XPS analyses confirmed that an amine-acid salt was formed in amine treated organosolv lignin. Application of XPS to copper amine treatment gave evidences of the formation of copper-amine-lignin complexes and amine-acid salts in organosolv lignin upon treatment. ESR spectra of copper-amine treated organosolv lignin confirmed that the structure of formed copper-amine-lignin complex is one mole copper complexed to two mole amines.

For copper-HDO amine treatment, XPS spectra demonstrated the formation of $Cu(HDO)_2$ precipitate. In addition, copper-amine complexes with lignin, and amine-acid salt were found to be present during fixation. ESR results supported the formation of the $Cu(HDO)_2$ precipitate in copper-HDO amine treated organosolv lignin.

Chapter 7

Reactions of holocellulose and pectin with copper-amine and copper-HDO amine solutions

7.1. Introduction

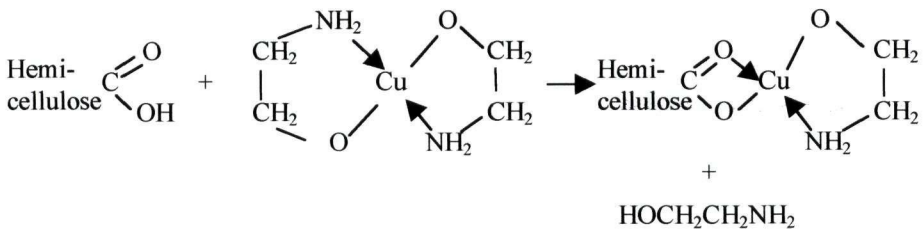
In defining wood composition, cellulose (40-50%) and hemicellulose (20-35%) are known collectively as holocellulose. Hemicelluloses are complex mixture of short chain polysaccharides which are either water or alkali soluble. The chemistry of hemicelluloses has been widely studied and has been found to be much more complicated than that of cellulose (Sjostrom, 1993; Whistler and Chen, 1991). In softwoods galactoglucomannans and arabinoglucuronxylans predominate, while in hardwoods glucuronoxylans and glucomannans occur most frequently. Softwood contains about 5-10% of arabinoglucuronxylan, which unlike galactoglucomannan, contains carboxylic acid groups substituted on the xylan side chain. Similarly, glucuronoxylan (15-30%) in hardwoods is the major hemicellulose to carry carboxylic acid groups.

The carboxyl group in hemicellulose is an important potential fixation site for copper in wood. The ion exchange with wood has been shown previously for copper(II) and zinc(II), as well as for quaternary ammonium compounds. Such reactions are strongly affected by the pH of the treating solution. Ion exchange capacity is much greater in high pH solution than from neutral or acidic solutions (Cooper, 1991; Jin and Preston, 1991). The availability of protons on the carboxylic acid functional groups of hemicelluloses can lead to simple copper chelated compounds being formed in wood.

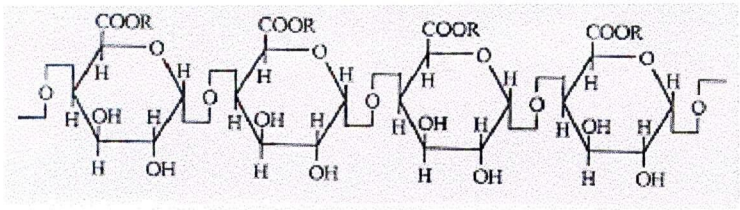
There are a few research reports currently available about copper-hemicellulose reactions. Xie (1994) isolated holocellulose from wood to investigate its reaction with ammoniacal copper solution. A comparison of the FTIR spectra of untreated and treated holocellulose showed the loss of the carboxyl group peak at 1734 cm^{-1} and the appearance of a strong new peak at 1670 cm^{-1}. This new peak could be assigned either to an amine or an amide. This observation suggested the possibility that the carboxyl group in hemicellulose could be involved in a condensation reaction with the ammonia, to form an amide. The role of this amide (if formed) remains unclear. Lebow and Morrell (1995) examined the reaction of xylan (a polyose model compound, which is the primary hemicellulose in hardwood) with ammoniacal copper zinc arsenate, to study the role of hemicellulose in the fixation chemistry of ACZA. Copper adsorption from ACZA solution onto xylan was more rapid than that observed for sapwood or cellulose samples, confirming the role of the uronic acid groups in binding copper.

The fixation reaction of copper amine solution and hemicellulose was also discussed by Thomason and Pasek in 1997. They observed that the amount of adsorbed copper decreased when the number of acid groups in wood was reduced by heating, and concluded that the adsorbed copper was bound to the carboxylic acid groups within hemecellulose. Kamdem and Zhang (2000) recently confirmed the important role of hemicellulose in copper adsorption during copper amine treatment, and suggested that the carboxylic acid groups in hemicelluloses are one of the major bonding sites for copper (Zhang and Kamdem, 2000). It is important to understand the role of hemicellulose in the fixation of copper.

A possible mechanism for the reaction of copper amine with hemicellulose (Thomason and Pasek, 1997) is shown below:



An unexplored reaction is the role of pectin in wood. Pectin (also called pectic substances) is present throughout the cell wall and occurs in the highest concentration in the middle lamella (Saka, 1990). Pectin is a group of heteropolysaccharides, and known as a component of connecting tissue between the wood fibers (Raven et. al., 1986). The basic building unit of pectin is D-galacturonic acid and/or D-galacturonic acid methyl ester, connected by 1-4-α linkages as shown below (Pigman and Geopp, 1948).



R=H or CH_3

The potential reactions between hemicellulose recovered from Scots pine with copper-amine and copper-HDO amine solutions were investigated in this study to isolate their reactions from those of other wood structural components. In order to find out whether a pectin reaction could occur in wood, the interactions of pectin and copper-amine and copper-HDO amine solutions were also studied. FTIR, ESR, and XPS were used to confirm the nature of the complexes formed among copper, amine, and carboxylic acid groups. In this part of research, xylan was attempted to model hemicellulose glucuronic acid reactions with copper-amine and copper-HDO amine solutions.

7.2. Materials and methods

7.2.1. Reactions of xylan with copper-amine and copper-HDO amine solutions

Hardwood birch xylan and xylan from oat spelts (Aldrich Co.) were used in this series of experiments to investigate the potential reactions between the carboxylic acid group in xylan and copper or amine in copper-amine and copper-HDO amine solutions.

7.2.2. Reactions of pectin with copper-amine and copper-HDO amine solutions

Pectin from citrus fruits was purchased from Aldrich Co. A 2.5 g aliquote of pectin was weighed into a 500 ml beaker. Warm (75°C) distilled water (250 ml) was added to the beaker, and then stirred until the pectin was completely dissolved. Copper amine or copper-HDO amine solution (20 ml) was added, dropwise to the pectin solution with stirring. The beaker was allowed to sit on the bench for three days, before being rotovapored to dryness for analyses by FTIR, XPS and ESR. The solutions of pectin and copper-HDO amine contained a small amount of purple precipitate. This precipitate was collected by filtration, and washed with warm distilled water. The purple solid was then identified by FTIR.

7.2.3. Preparation of holocellulose with copper-amine and copper-HDO amine solutions

Holocellulose from Scots pine was prepared according to the Tappi T 249 cm-85 procedure.

Scots pine sapwood was ground into 20 mesh sawdust. The sawdust was extracted with dichloromethane for overnight. After completing the extraction, the sawdust was collected in a petri dish for air dried. A 2 g sample of air-dried extractive-free Scots pine wood meal was placed in a centrifuge tube. 28 ml aliquote of buffer solution (60 ml acetic acid and 1.3 g sodium chloride in one liter distilled water) and 12 ml of 20% sodium chlorite solution were then added. The tube containing the mixture was placed in a constant temperature shaking bath (at 50 ^{o}C) overnight. Afterwards, the solution was cooled by placing the tube in ice before the solution was transferred to a Buchner funnel lined with filter paper. The solid on the filter paper was washed first with 1% acetic acid, and then with acetone (15 ml). The samples were air-dried at ambient temperature for one week prior to use.

7.2.4. Reactions of holocellulose with copper-amine and copper-HDO amine solutions

About 2 g Scots pine holocellulose and 50 g of 1.0 % (expressed as CuO) copper amine or copper-HDO amine solution were added to 100 ml beakers. The beakers were sealed by parafilm® and agitated on a shaker for 24 hours. After the agitation, samples were filtered through glass fibers and washed continuously with deionized water until the conductivity of the eluent water was constant and matched that of deionized water. This washing was carried out in order to minimize physical adsorption of copper on the surface of the treated samples. The samples were then air-dried for two weeks.

7.2.5. Spectroscopic analysis

FTIR spectra were recorded on a Perkin-Elmer 1600™ spectrophotometer over the range 4000 cm^{-1} to 400 cm^{-1}. Air-dried samples were mixed with KBr to make KBr discs before spectrum collection. FTIR spectrum was acquired for a total of 4 scans with a resolution of 4 cm^{-1}.

The ESR spectra were collected using a Bruker ECS-160™ spectrometer. The ESR spectra were recorded at room temperature. The treated holocellulose and pectin solids were examined directly. The parameters used for recording ESR spectra were the same as those used for examining treated wood (See Table 4-2).

Compressed pellets were prepared for the XPS measurement, which were obtained in a Leybold Max200™ spectrometer, applying the same operating parameters as described in Section 4.2.3 for examination of thin wood sections.

7.3. Results and discussion

7.3.1. FTIR analysis

7.3.1.1. Reaction of xylan with copper-amine and copper-HDO amine solutions

FTIR spectra of xylans are shown in Figure 7-1. Neither birch xylan nor xylan from oat spelts showed the carboxylic acid stretching vibration at 1730 cm^{-1}. Since these two sources of xylans did not contain any free carboxylic acid groups, it was not possible to use them to assess the potential reaction of glucuronic acid in hemicelluloses with copper-amine or copper-HDO amine solutions. Instead, reactions were conducted with holocellulose derived from Scots pine.

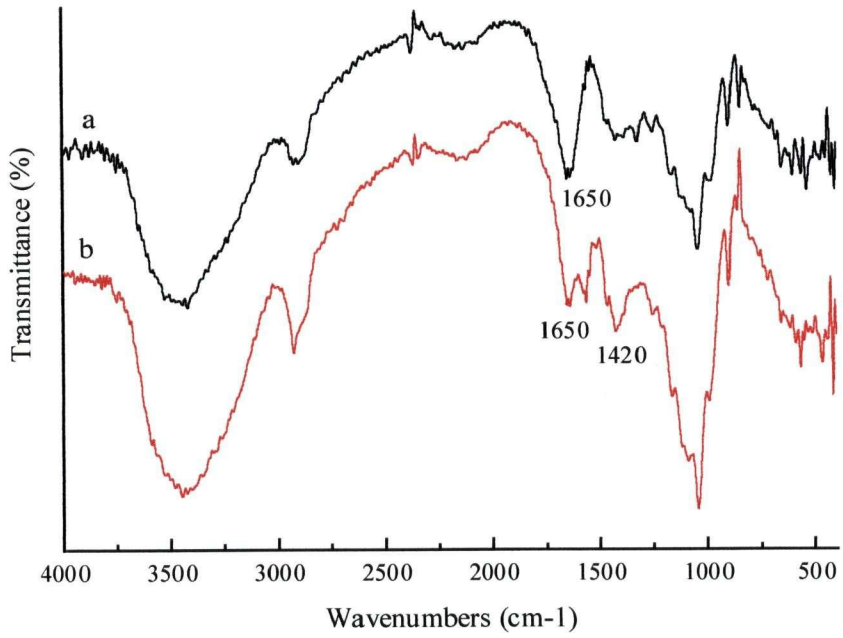


Figure 7-1: FTIR spectra of a) xylan from birch, and b) xylan from oat spelts.

7.3.1.2. Reactions of holocellulose with amine, copper-amine and copper-HDO amine solutions

Comparison of the FTIR spectra of untreated and amine treated holocellulose (Figure 7-2) showed that the peak at 1744 cm^{-1} had disappeared. Since the peak at 1744 cm^{-1} is the characteristic stretching vibration of carboxylic acid in holocellulose, the loss of this peak confirmed the reaction of the carboxyl acid (-COOH) proton with amines, to form an amine acid salt. This should have caused the peak at 1640 cm^{-1}, associated with carboxylate stretching vibration to increase. However, this peak did not appear to increase but slightly decreased. Probably the reason for this is that carboxylate groups

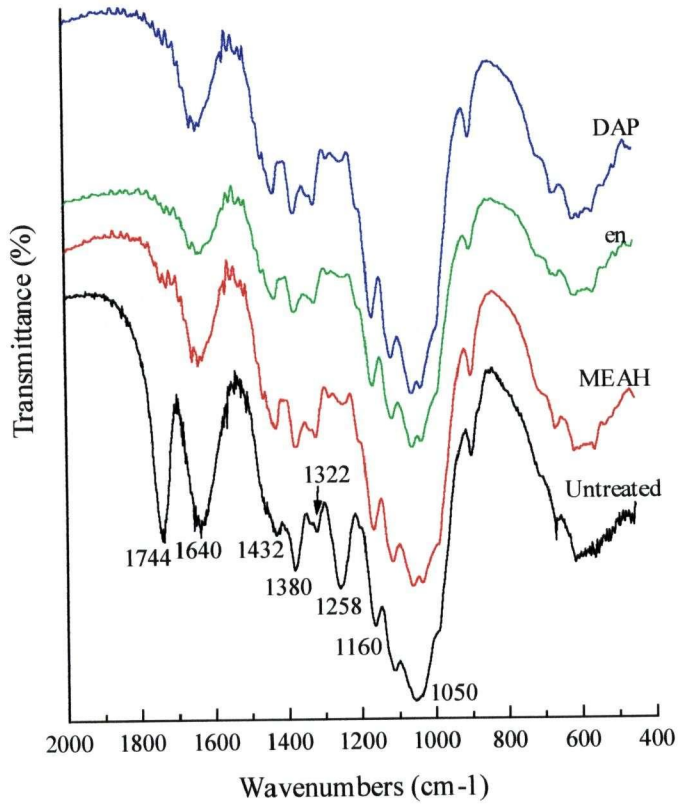


Figure 7-2. FTIR spectra of untreated and amine treated holocellulose.

associated with the O-acetyl groups in hemicellulose, are very easily cleaved by alkaline solutions. For all amine treatments, the peak at 1258 cm^{-1} is greatly reduced. This peak is related to C-O-C vibration in hemicellulose. The reduction of this peak is interpreted to indicate the hydrolysis of the ether group in hemicellulose under the highly alkaline conditions present. The peak at 1380 cm^{-1}, due to the C-H deformation, was slightly decreased. This caused the peak at 1432 cm^{-1} to be better resolved. The cause of the change in the peak at 1380 cm^{-1} is not clear. It is likely related to the cleavage of the ether and acetyl groups in hemicelluloses under the strong basic conditions or the reaction of carboxylic acid group with the amine.

FTIR spectra of copper-amine and copper-HDO amine treated holocellulose are present in Figures 7-3 to 7-5. They show changes similar to those observed for amine treated holocellulose, with no significant shift in frequency for the copper complex compared with those found in the amine treated holocellulose spectra. The major changes are the almost complete disappearance of the peak at 1744 cm^{-1}, slight decrease of the peak at 1640 cm^{-1}, and reduction of the peak at 1258 cm^{-1}. However, it is not clear whether these changes arise from the interactions of holocellulose with copper-amine or with amine alone. The FTIR measurements do not allow identification of any copper complex formation or $Cu(HDO)_2$ precipitation.

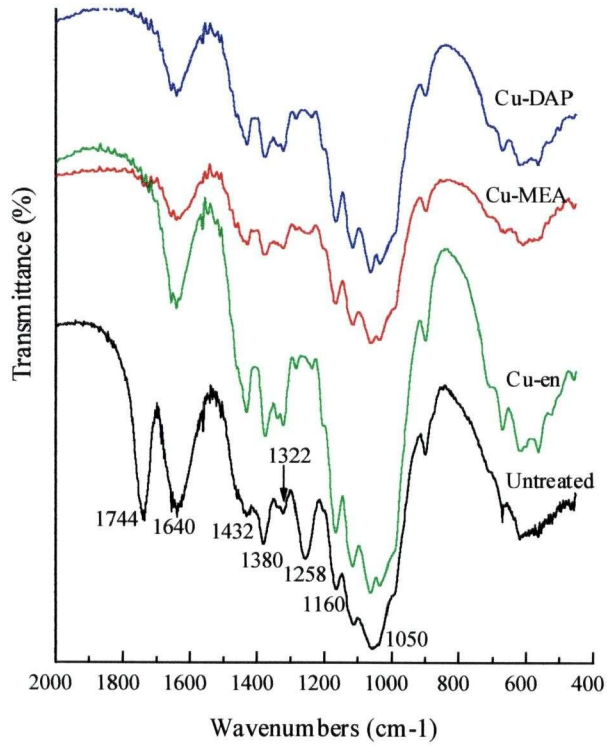


Figure 7-3. FTIR spectra of untreated and copper-amine treated holocellulose.

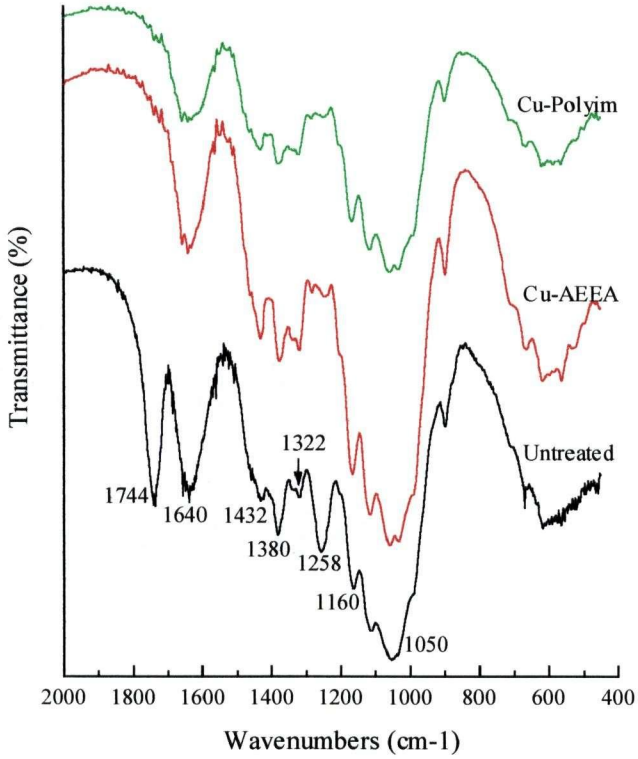


Figure 7-4. FTIR spectra of untreated and copper-amine treated holocellulose.

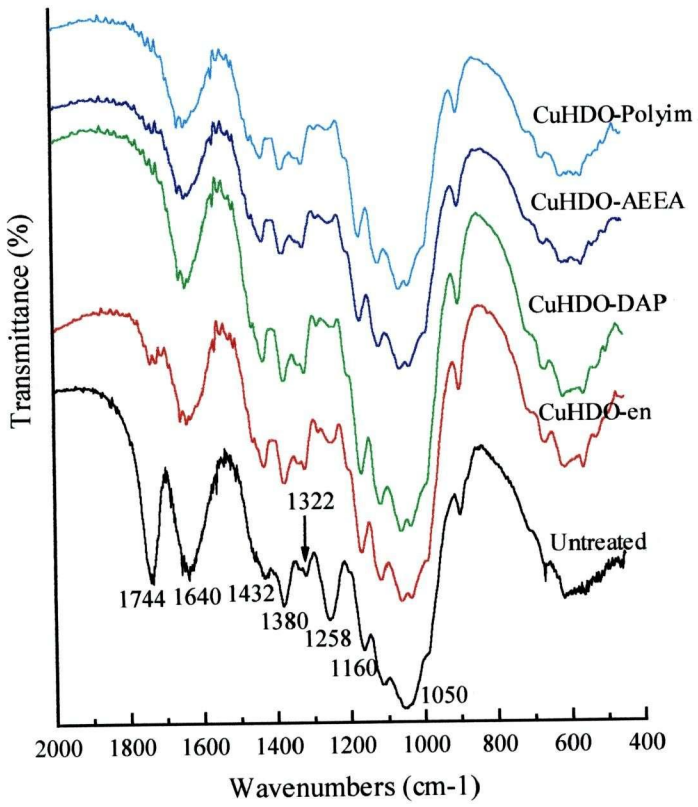


Figure 7-5. FTIR spectra of untreated and copper-HDO amine treated holocellulose.

7.3.1.3. Reactions of pectin with amine, copper-amine and copper-HDO amine solutions

The most common units of pectic polysacchrarides consist of D-galactosyluronic acid and D-galactose, L-arabinose, and L-rhamnose residues. Figure 7-6 shows the FTIR spectra of untreated pectin and amine treated pectin. Peaks at 1744 and 1624 cm^{-1} are derived from C=O stretching vibrations from COOH and COO^- respectively. The combination of these peaks with three peaks around 1416, 1328 and 1236 cm^{-1} (OH stretching vibrations) is characteristic for uronic acids (Veen and Ent, 1994). After the pectin was treated with the different amine solutions, the carboxylic acid peak disappeared and the intensity of the peak at 1624 cm^{-1} increased because of the conversion of the carboxylic acid into the carboxylate. The absorption of N-H banding in amine-acid salt occurs in the same region. The peak at 1416 cm^{-1} substantially increased, and the relative intensity of peak at 1328 cm^{-1} and peak at 1236 cm^{-1} is reversed. All these changes are associated with the reactions with the uronic acid in pectin, suggesting that the uronic acid groups are the major active sites for bonding amine with pectin.

The copper-amine and copper-HDO amine treated pectin showed very similar changes in the FTIR spectrum observed in the spectra of the corresponding amine treatment (Figures 7-7 to 7-9). The lack of definitive changes in the FTIR spectra, prevents the role of copper and HDO in the interaction with pectin being identified by FTIR analysis.

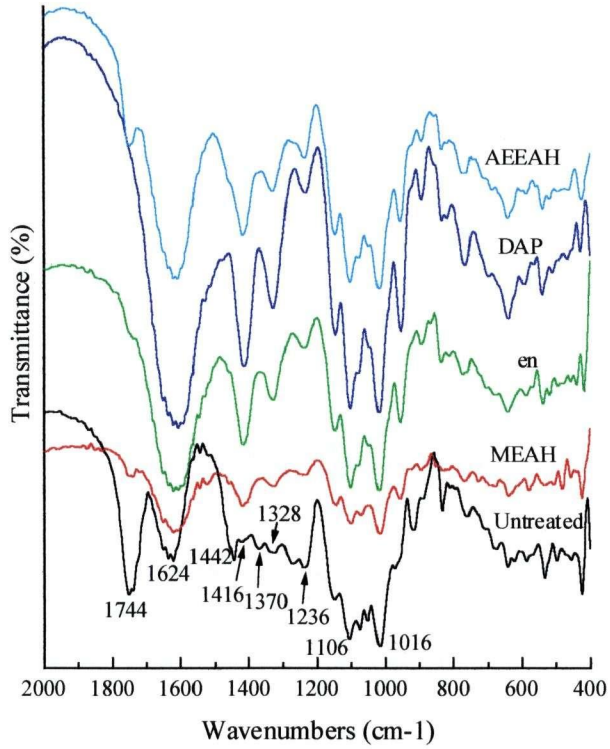


Figure 7-6. FTIR spectra of untreated and amine treated pectin.

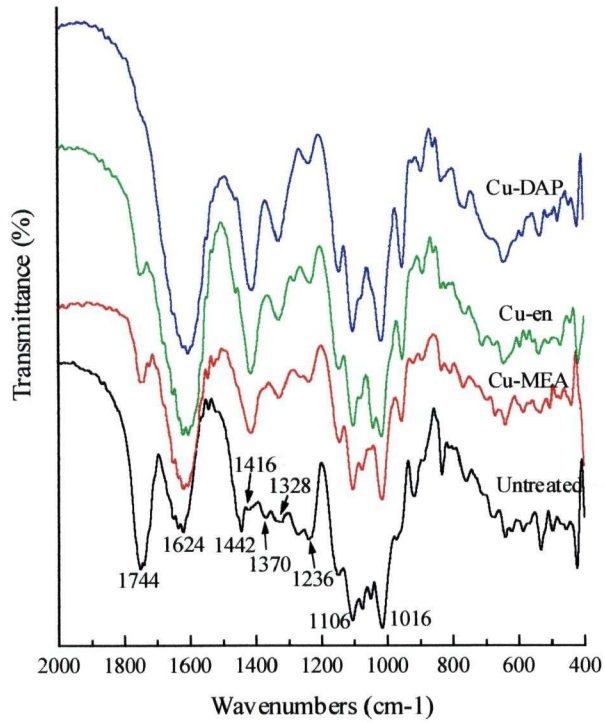


Figure 7-7. FTIR spectra of untreated and copper-amine treated pectin.

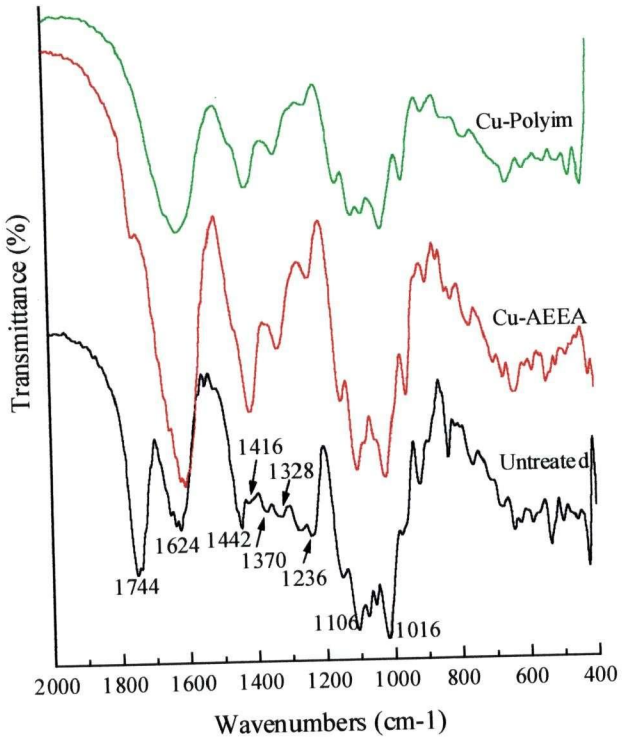


Figure 7-8. FTIR spectra of untreated and copper-amine treated pectin.

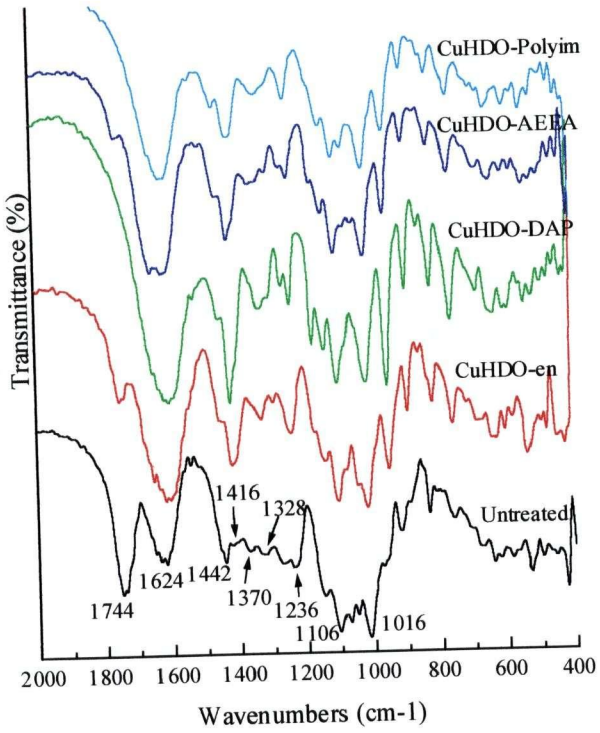


Figure 7-9. FTIR spectra of untreated and copper-HDO amine treated pectin.

The purple precipitates formed during the reactions of pectin with copper-HDO amine solutions, were filtered and examined by FTIR analysis. The FTIR spectrum obtained was identical to that of pure $Cu(HDO)_2$ (Figure 7-10). This confirmed the formation of $Cu(HDO)_2$ during the interaction between pectin and copper-HDO amine solutions. The precipitation was expected since it can be easily brought about by the neutralization of the basic copper-HDO amine solution with the acidic pectin solution directly.

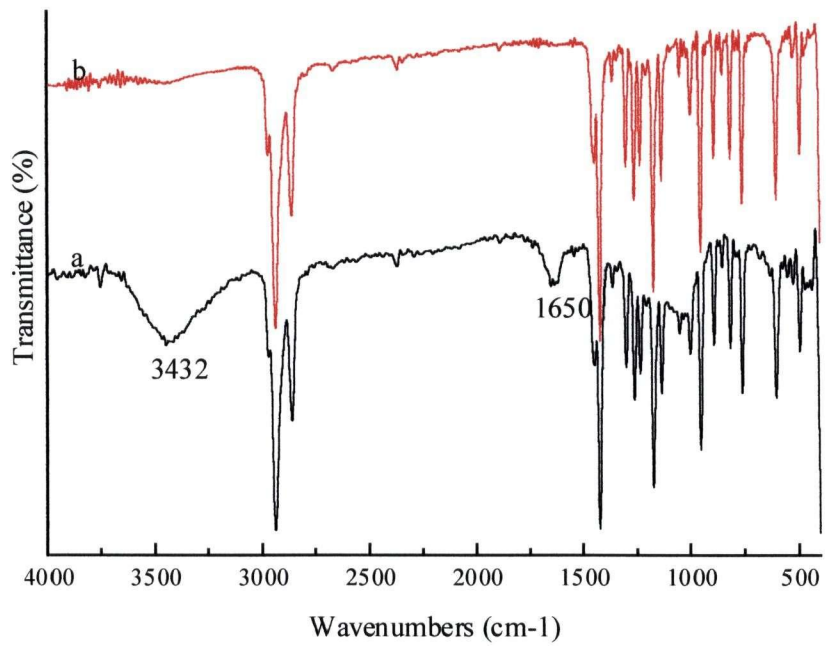


Figure 7-10. FTIR spectra of a) $Cu(HDO)_2$ and b) purple precipitate.

7.3.2. XPS analysis

7.3.2.1. Reactions of holocellulose with amine, copper-amine, and copper-HDO amine solutions

The C1s spectrum of holocellulose displays three partially resolved peaks (Figure 7-11). The large number of C-O-C and C-O-H linkages in cellulose and hemicelluloses results in the dominance of the C2 peak in the C1s spectrum of holocellulose, while the small number of uronic acid groups combined with O-C-O linkage in hemicellulose gives rise to the C3 peak. The small C1 peak arises from the C-C bonding, and is assumed to be due to a small amount of residual lignin in the holocellulose (Westermark, 1999). After treating with monethanolamine and ethylendiamine, C3 slightly enhanced (Figure 7-11, Table 7-1). This is probably caused by the stopping reaction of peeling under the strong alkali condition. The strong alkaline solution could convert the end groups in polysaccharides to a carboxylic acid (Sjostrom, 1993). In general, the peak areas of C1 and C3 are very small for all of the amine treatments, and change of C1 and C3 is slight (Table 7-1). The peeling reactions, the presence of a small amount of lignin, the addition of C1 from the amine (in the case of DAP) and peeling reaction, and the variability of the XPS spectrum fitting could be considered to account for the slight changes for C1 and C3.

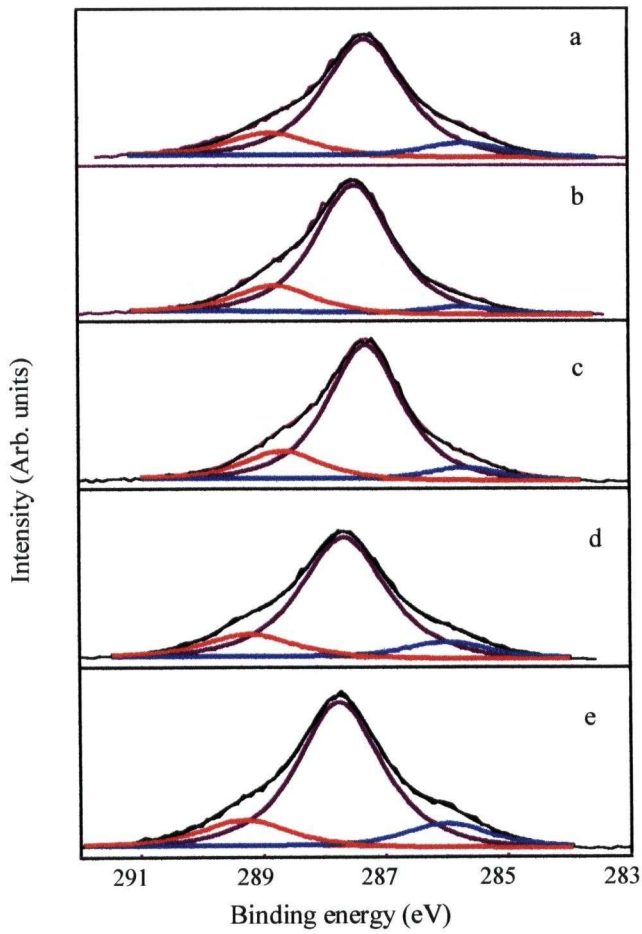


Figure 7-11. XPS C1s spectra of a) holocellulose, b) MEAH treated holocellulose, c) en treated holocellulose, d) DAP treated holocellulose, and e) AEEAH treated holocellulose.

Table 7-1.The binding energies of C1s and N1s spectra for untreated and amine treated holocellulose.

Sample ID	C1s (eV)			N1s (eV)
	C1	C2	C3	
Holocellulose	285.00 (3916*)	286.77 (31075)	288.49 (5956)	
MEAH treated	285.00 (2075)	286.97 (32050)	288.42 (6413)	-----**
en treated	285.00 (3000)	286.78 (30458)	288.29 (6230)	-----
DAP treated	285.00 (3684)	286.67 (26460)	288.21 (4973)	400.53 (888)
AEEAH treated	285.00 (4874)	286.75 (29285)	288.31 (5312)	400.48 (1029)

* Peak area
** Not detectable

The N1s peak for MEAH and en treated holocellulose was not detectable. This might be associated with the terminal reaction of peeling of holocellulose with MEAH and en. The carboxylic acid products formed after peeling reaction can be stabilized in alkaline solution, rather than further reacting with the amines. Thus amine would be washed away by distilled water, and not observable. For DAP and AEEAH treatments, the nitrogen peak is clearly visible (Figure 7-12). The binding energy of the nitrogen peak is located at ca. 400.5 eV (Table 7-1). This is in agreement with the value reported for amine-acid salt of 400.4 to 401.2 by Nordberg et. al. (1967). It is suggested that the uronic acid groups in hemicellulose are able to react with DAP and AEEAH to form amine-acid salts.

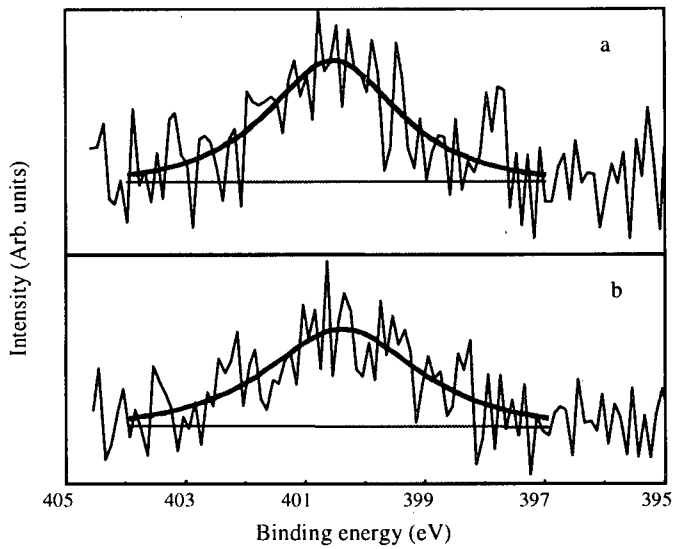


Figure 7-12. XPS N1s spectrum of a) DAP and b) AEEAH treated holocellulose.

In copper-amine treated holocellulose, two nitrogen peaks were observed. The peak of N1 is located at 399.2 ~ 400.2 eV. Based on the binding energy of this nitrogen it was assigned to that from copper-amine compounds. The fixation reaction between carboxylic acid in holocellulose and copper-amine has been suggested by several authors (Kamdem and Zhang, 2000; Thomason and Pasek, 1997; Zhang and Kamdem, 2000), and this result confirms that such a copper-amine complex was formed during treatment. The second nitrogen peak N2 with the higher binding energy (400.4 ~ 401.21 eV) is consistent with that assigned to amine-acid salt (Table 7-2). This suggests that the excess

amine in the copper-amine formulation (in the case of Cu-MEA and Cu-Polyim solution), and amine released during copper complex formation, reacts with the carboxylic acid to form an amine acid salt. However, only one nitrogen peak, associated with the copper-amine complex, was found in Cu-AEEA treatment, suggesting that in this case the formation of amine-acid salt is less likely.

The XPS spectra for copper again showed signs of copper(I) formed by reduction during the XPS measurement. The higher binding energy of Cu2p (which is the major peak), at 934.2 ~ 935.1 eV, compares well with those presented earlier for the copper-amine wood complex, supporting the assignment of one of the nitrogen peaks to a copper-amine complex.

The copper-HDO amine treated samples did not give consistent N1s spectra. The presence of $Cu(HDO)_2$ precipitate was observed in CuHDO-en, CuHDO-DAP and CuHDO-AEEA treated samples, based on the characteristic nitrogen peak (N3) with the average binding energy of ca. 402.6 eV (which is actually comprised of two peaks at ca. 402.0 and 402.9 eV). This confirmed that the precipitation of $Cu(HDO)_2$ is dominant in the treatment of diamine-copper systems. This peak was not found after the CuHDO-Polyim treatment. The formation of copper-amine complex with holocellulose was also observed in CuHDO-en, CuHDO-AEEA and CuHDO-Polyim indicated by the binding energy of ca. 400.0 eV. In the CuHDO-DAP and CuHDO-Polyim treated samples the formation of amine acid salt was confirmed by the presence of the binding energy at ca. 400.5 eV. For the CuHDO-DAP treatment, the low binding energy located at 398.8 eV, which is in good agreement with the reported value for the free amine, was due to the

presence of free amine in the CuHDO-DAP treated sample. The non-uniform presentation of different nitrogen species in copper-HDO amine treatment may arise from the relative amount of different nitrogen species fixed in holocellulose, and their movement to the sample surface.

It is interesting to note that the binding energy of copper is consistent with the assignment of the nitrogen in the copper-HDO amine treated samples. For CuHDO-en, CuHDO-DAP and CuHDO-AEEA treatments, the binding energy of copper is ca. 935.6 eV, which is in good agreement with the value recorded for the pure $Cu(HDO)_2$ solid. On the other hand, the CuHDO-Polyim treated sample showed a copper binding energy of 934.88 eV, which compared well with the binding energy of copper in the copper-amine complex.

Table 7-2. The binding energies of N1s and Cu2p spectra for copper-amine and copper-HDO amine treated holocellulose.

Sample ID	N1s (eV)			Cu2p (eV)	
	N1	N2	N3	Cu1	Cu2
Cu-MEA	399.41	400.69		933.15	935.06
Cu-en	399.26	400.49		933.16	934.38
Cu-DAP	399.75	401.21		933.07	934.16
Cu-AEEA	400.19			933.12	934.79
Cu-polyim	399.96	400.57		933.10	934.97
CuHDO-en	400.09		402.70	933.11	935.35
CuHDO-DAP	398.80	400.57	402.60	933.32	935.60
CuHDO-AEEA	400.25		402.59	933.15	935.69
CuHDO-Polyim	399.60	400.46		932.80	934.88

7.3.2.2. Reactions of pectin with copper-amine and copper-HDO amine solutions

The N1s and Cu2p binding energies for amine, copper-amine and copper-HDO amine treated pectin are given in Table 7-3. Two nitrogen peaks were easily observed in all treatments, as illustrated in Figure 7-13. For amine treated pectin, it is suggested that two different products are formed after treatment, based on the XPS N1s results (Table 7-3). The peak at ca. 399.7 eV is due to the interaction of the amine with the hydroxyl groups in pectin (for example -OH on C2 or C3), which could be activated during treatment with a highly basic solution. The N1s peak at 401.2 ~ 401.6 eV is consistent with those values observed for amine-acid salts, and presumably arises from a reaction with the carboxylic acid group in pectin.

The N1s spectra for the copper-amine treatments showed similar binding energies to those observed for amine treatments (Table 7-3). Whether the nitrogen in amine formed donor bonds to copper or to interact with the protons on the hydroxyl group in pectin, can not be identified by the results from N1s XPS, since these two reactions generate the binding energy for nitrogen in the same region. However, the Cu2p XPS data support the former reaction, the formation of a copper-amine-pectin complex. The binding energy of nitrogen located at ca. 400.3 ~ 401.3 eV in copper-amine treated samples suggests the formation of amine-acid salts during treatment. This is caused by the interaction of residual amine and carboxylic acid groups in pectin.

For copper-HDO amine treated pectin, the nitrogen peak at the higher binding energy (ca. 402.3 eV), which is actually comprised of two peaks at ca. 402.0 and 402.9 eV, was assigned to $Cu(HDO)_2$ precipitate (Table 7-3). This confirmed the precipitation

reaction during copper-HDO amine treatment with pectin. The formation of $Cu(HDO)_2$ precipitate was also supported by the observation of the purple solid during the reaction, which was identified as $Cu(HDO)_2$ by FTIR. The lower binding energy present at 399.6 ~ 400.1 eV arose from the interaction of the residual copper with the amine with pectin to form a copper-amine-pectin complex. The binding energy of copper was located at ca. 934.6 ~ 935.2 eV, (Table 7-3), which together with the satellite peak confirmed the presence of copper(II) pectin complexes.

Table 7-3. The binding energies of N1s and Cu2p spectra for amine, copper-amine and copper-HDO amine treated pectin.

Sample ID	N1s (eV)		Cu2p (eV)	
	N1	N2	Cu1	Cu2
MEAH	400.17	401.56		
en	399.90	401.59		
DAP	399.68	401.29		
AEEAH	399.65	401.20		
Cu-en	399.69	401.29		934.28
Cu-DAP	399.61	400.94	933.19	934.58
Cu-AEEA	399.28	400.25	932.55	934.63
Cu-polyim	399.89	401.05	933.66	934.81
CuHDO-en	399.78	402.23	932.33	935.27
CuHDO-DAP	400.13	402.42	933.32	935.03
CuHDO-AEEA	399.93	402.49	932.91	935.17
CuHDO-Polyim	399.64	402.31	932.40	934.64

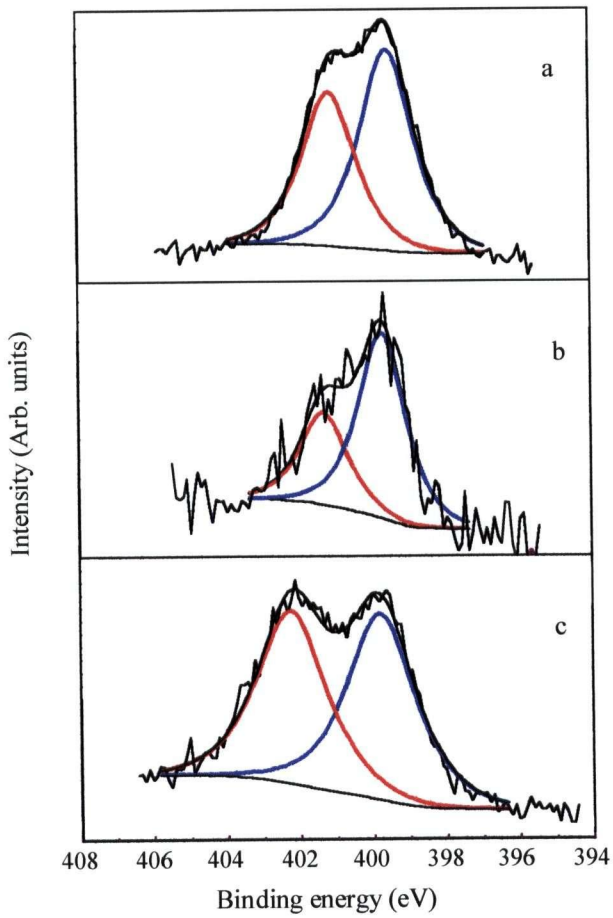


Figure 7-13. XPS N1s spectra of a) en treated, b) Cu-en treated, and c) CuHDO-en treated pectin.

7.3.3. ESR analysis

7.3.3.1. Reactions of holocellulose with copper-amine and copper-HDO amine solutions

The ESR esults from the reactions between holocellulose and copper-amine solutions are shown in Table 7-4. The four hyperfine splittings in the $g_{//}$ area were easily observed except for Cu-Polyim treated sample, in which no hyperfine structure was visible. For Cu-MEA treatment, only one copper species was found in the ESR spectrum. The values of $g_{//}$ and $A_{//}$ compared well with those for a central copper complexed to two nitrogen atoms (from the amine) and two oxygen atoms (from holocellulose or amine), indicating one mole of copper is bound to two moles of monoethanolamine. Unlike the ESR results from the interactions of copper-amine solutions with organosolv lignin, in which only one copper species was found, for the diamine-copper treatments (Cu-en, Cu-DAP and Cu-AEEA), two copper species were present in the treated holocellulose (Figure 7-14). This supports the conclusion that two different forms of copper were present in the treated holocellulose. One of the copper species with the higher $g_{//}$ and lower $A_{//}$, arises from copper bound to two nitrogen atoms and two oxygen atoms in a plane arrangement. The values of $g_{//}$ and $A_{//}$ for the second copper species are consistent with the assigned copper coordination in which the central copper is bonded to four nitrogen atoms, i.e. one mole of copper is attached by two moles of amines. The ESR results from the reactions between copper-amine solutions and holocellulose are quite similar to those from the interactions with wood, implying holocellulose plays a significant role in the fixation of copper in wood.

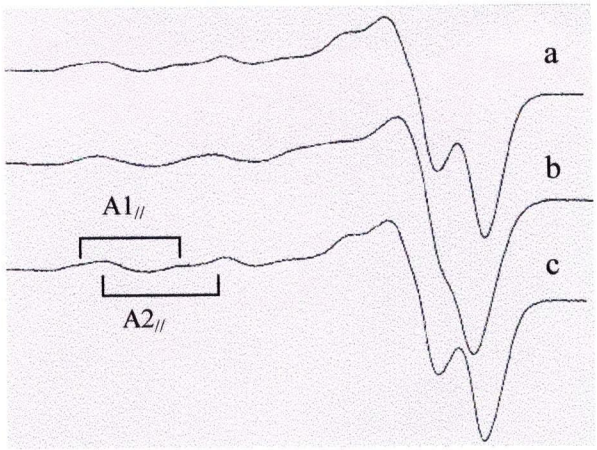


Figure 7-14. ESR spectra of a) Cu-en treated, b) Cu-DAP treated, and c) Cu-AEEA treated holocellulose ($A1_{//}$ is for copper species (1), and $A2_{//}$ is for copper species (2)).

Only one copper species was observed in the ESR spectrum of copper-HDO amine treated holocellulose. High $A_{//}$ and low $g_{//}$ values (Table 7-4) are consistent with the results from the copper-HDO amine treated wood, as well as treated organosolv lignin. The copper species formed during copper-HDO amine treatment was assigned to the $Cu(HDO)_2$ precipitate. However, $g_{//}$ and $A_{//}$ assigned for copper species bound to four nitrogen atoms, occur in the same region as those observed for $Cu(HDO)_2$. It is not possible to use the ESR spectra alone to identify whether copper amine complex or $Cu(HDO)_2$ precipitate is formed in copper-HDO amine treatments. Based on the XPS results, the copper species formed in copper-HDO diamine treated holocellulose (CuHDO-en. CuHDO-DAP, and CuHDO-AEEA) is preferably assigned to $Cu(HDO)_2$ precipitate, while that formed in CuHDO-polyim treatment is to copper complexed to two moles of amine.

Table 7-4. ESR spectral parameters of $g_{//}$ and $A_{//}$ for copper-amine and copper-HDO amine treated holocellulose.

Sample ID	$g_{//}$	$A_{//}$
Cu-MEA	2.256	169
Cu-Polyim	---*	---
Cu-en (1)	2.260	171
Cu-en (2)	2.200	198
Cu-DAP (1)	2.254	172
Cu-DAP (2)	2.208	189
Cu-AEEA (1)	2.252	170
Cu-AEEA (2)	2.208	187
CuHDO-en	2.202	194
CuHDO-DAP	2.230	189
CuHDO-AEEA	2.206	188
CuHDO-Polyim	2.190	190

* No hyperfine structure

7.3.3.1. Reactions of pectin with copper-amine and copper-HDO amine solutions

The representative ESR spectra of copper amine and copper-HDO amine treated pectin were presented in Figure 7-15. For all treatments, only one copper species was found in the ESR spectra. The electronic parameters of $g_{//}$ and $A_{//}$ for copper monoamine treatments (Cu-MEA and Cu-Polyim) are similar with higher $g_{//}$ and lower $A_{//}$ values. This is consistent with the formation of the copper complex coordinated to two nitrogen atoms, indicating that the dominant copper species in Cu-MEA and Cu-Polyim treated pectin is a copper complex with a mole ratio of copper to amine of 1:2. All the diamine-

copper treatments (Cu-en, Cu-DAP and Cu-AEEA) can be grouped together with the higher $A_{//}$ and lower $g_{//}$ values. The electronic data is in agreement with four nitrogen atoms complexed to the Cu(II) central atom in a distorted octahedral environment, suggesting the formation of copper-amine complexes with two moles of amine and one mole of copper. The ESR data of copper-HDO amine treated pectin displayed a uniform picture for all formulations. Again, it is not possible to confirm, whether the copper-amine complex or $Cu(HDO)_2$ precipitate, is formed in copper-HDO amine treatments by ESR analysis alone, since the $g_{//}$ and $A_{//}$ values assigned for copper species, bound to four nitrogen atoms, occur in the same region as those observed for $Cu(HDO)_2$. Based on the findings in XPS analysis of copper-HDO amine treated pectin, it is tentatively concluded that the values of $g_{//}$ and $A_{//}$ reflect the formation of $Cu(HDO)_2$ precipitate during the treatment, confirming that the precipitation of $Cu(HDO)_2$ is one of the dominant reactions for copper.

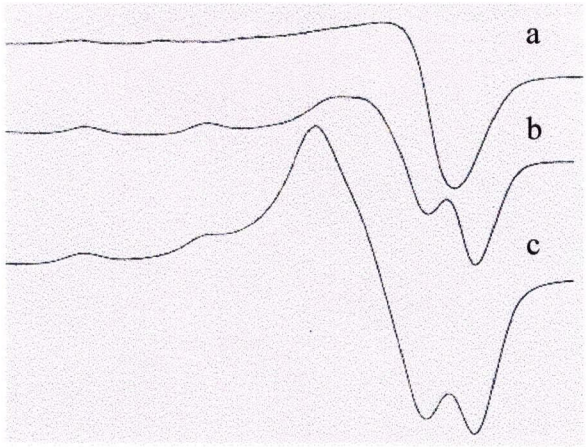


Figure 7-15. ESR spectra of a) Cu-MEA treated, b) Cu-en treated, and c) CuHDO-en treated pectin.

Table 7-5. ESR spectral parameters of $g_{//}$ and $A_{//}$ for copper-amine and copper-HDO amine treated pectin.

Sample ID	$g_{//}$	$A_{//}$
Cu-MEA	2.257	169
Cu-Polyim	2.258	167
Cu-en	2.202	186
Cu-DAP	2.206	186
Cu-AEEA	2.201	186
CuHDO-en	2.190	191
CuHDO-DAP	2.208	186
CuHDO-AEEA	2.209	189
CuHDO-Polyim	2.191	188

7.4. Conclusions

FTIR spectroscopy study indicated that the interactions of holocellulose and pectin with amine, copper amine and copper-HDO amine solution, occurred primarily through the carboxylic acid functional group in hemicellulose and pectin.

An amine-acid salt was formed in amine treated holocellulose and pectin, which was confirmed by FTIR and XPS analyses. In addition to the formation of amine-acid salts, in copper-amine treated holocellulose and pectin, it was suggested by XPS N1s and ESR spectra that copper-amine complex was formed during treatment. ESR provided further evidences for the formation of copper-amine complexes with the mole ratio of copper and amine 1:2 for all pectin reactions. However, for the interactions of holocellulose and copper-diamine systems (Cu-en, Cu-DAP and Cu-AEEA), two copper species were present, identified as one mole of copper coordinated to one mole of amine or two moles of amine by ESR measurement.

ESR analysis alone is unable to confirm whether copper amine complex or $Cu(HDO)_2$ precipitate is formed in copper-HDO amine treatments. However, XPS measurements confirmed that the precipitate of $Cu(HDO)_2$ was formed in all copper-HDO amine treated samples.

Chapter 8

Reactions of heartwood extractives with copper-amine and copper-HDO amine solutions

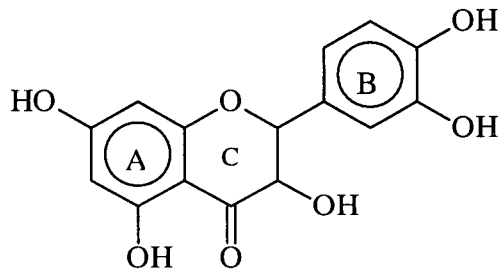
8.1. Introduction

Wood extractives, a minor fraction (<5%) of wood mass, are soluble in neutral organic solvents or water. They are found in parenchyma cells and resin canals, and are not considered part of the cell wall components. Wood extractives can be classified into three main groups: a) terpenoids and steroids, b) phenolic compounds, and c) fats and waxes (Sjostrom, 1993). Although in general the quantity of extractives in woods is small, their presence can have a significant effect on wood utilization and properties. Extractives often affect wood characteristics, such as color, odor, durability, gluability, and finishing. They also have a significant influence on the wood preservation industry. For instance, CCA treatment of Douglas-fir heartwood is very difficult to achieve, due to the interaction of chromium and copper with the polyflavonoid extractives. The extractive taxifolin, in Douglas-fir is responsible for the black color when Douglas-fir heartwood is reacted with ammoniacal copper solution.

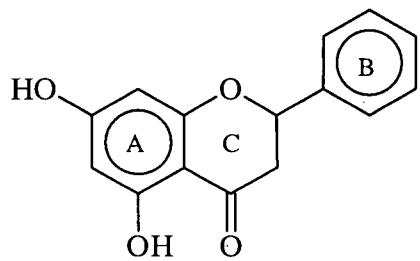
Lebow and Morrell (1995) showed that, among the wood components in Douglas-fir, the second highest copper adsorption in ACZA was with heartwood. They suggested that the phenolic extractives could react with the metal components in ammoniacal copper solutions. This confirmed previous research which demonstrated that ammoniacal copper solutions reacted with taxifolin in Douglas-fir heartwood to produce a dark black water-insoluble copper-ammonia-taxifolin complex (Ruddick and Xie, 1994). However,

the structure of the copper taxifolin complex could not be determined. It was also not possible to predict whether a similar reaction would take place between amine-copper solutions and taxifolin.

As part of the overall research strategy to better understand the fixation chemistry of copper amine preservatives, their reaction with extractives in Douglas-fir and Scots pine was investigated. Reaction between taxifolin and the ammoniacal copper solution has been well characterized (Ruddick and Xie, 1994), and could, therefore, form the basis for understanding similar reactions involving copper-amine and copper-HDO amine solutions with taxifolin from Douglas-fir. The reaction products were identified by FTIR, ESR and XPS. Chrysin has a very similar molecular structure to taxifolin, differing only by the absence of the two hydroxyl groups on the B ring and the hydroxyl group on ring C (Figure 8-1). It was therefore selected to compare its reactions with those of taxifolin with a selection of copper-amine and copper-HDO amine solutions.



a



b

Figure 8-1. Molecular structures of a) taxifolin, and b) chrysin.

8.2. Materials and methods

8.2.1. Isolation of extractives from Scots pine heartwood and Douglas-fir heartwood with dichloromethane

Scots pine heartwood sawdust was provided by Dr. Wolman GmbH. About 8.0 g of air-dried Scots pine heartwood sawdust and Douglas-fir heartwood sawdust, were weighed into extraction thimbles. A cone-shaped filter paper with cotton was placed in the thimble to prevent the loss of sawdust during extraction. The thimble with the sample meal was placed in the Soxhlet apparatus, and extracted overnight with 200 ml of dichloromethane solvent, at a minimum rate of 4 siphonings per hour. After the extraction was completed, the solvent containing extractives were transferred to a round bottom flask, and rotovapored to dryness prior to reaction with different copper solutions (Tappi T 264 cm-97).

8.2.2. Isolation of taxifolin from acetone-extraction of Douglas-fir heartwood

Previous research has confirmed the recovery of taxifolin during acetone extraction (Xie, 1994). In order to isolate taxifolin from Douglas-fir heartwood, a 10.0 g portion of Douglas-fir heartwood sawdust was placed in an extraction thimble, and covered with a cone shaped filter paper and cotton. The thimble was placed in a Soxhlet extractor, and the sawdust was extracted with acetone (250 ml) for 24 hr. The extraction solution was concentrated on a rotary evaporator using a water-bath at 45 ^{o}C. Silica gel thin layer chromatography (TLC) with petroleum ether:acetone of 3:1 mixture as the developing agent was used to examine and monitor the composition of the extractives in

the eluent. The plate was subjected to ultraviolet light to reveal the components present. It was found that the acetone extraction contained a mixture of at least five compounds in addition to taxifolin.

Elution column chromatography with silica gel was used to isolate the taxifolin. A plug of cotton wool was placed in the bottom of the column (50 mm diameter glass tube). A petroleum ether-acetone mixture (3:2) was chosen as the eluting solvent, based upon previous research by Xie (1994) to obtain the maximum separation of the components.

The column was packed by adding silica gel slurry in the solvent mixture. After the column had been prepared, the solvent level was lowered to the top of the silica gel column by draining solvent from the bottom of the column. The acetone solution containing the extractives was applied carefully to the top of the silica gel column. The column was then eluted with the 3:2 petroleum ether and acetone mixture. In order to accelerate the elution, low air pressure was applied to the top of the column. The elution was monitored periodically by TLC on silica gel using petroleum ether : acetone (3:2) as the developing solvent. The TLC results were observed under UV light. The desired fractions containing only taxifolin (based on the TLC evaluation) were collected and consolidated. Evaporation of the eluent produced a cream white solid (taxifolin), which was filtered and dried.

The crude taxifolin was dissolved in a 50% ethanol-water solution (solid : solvent = 1:50), refluxed for 30 minutes, and immediately filtered. The filtered cake was washed three times with 50% warm ethanol solution, and then left on the bench to air-dry.

8.2.3. Preliminary reactions of extractives from Scots pine and Douglas-fir and copper solutions

The extractives from Scots pine and Douglas-fir were dissolved in methanol to form 2% solutions. A small sample (1ml) of each solution was reacted with 1 ml of each of the following copper solutions:

a) 1% $CuSO_4$

b) 1% $CuSO_4$ in ammonium hydroxide

c) 1% (expressed as Cu) Cu-MEA

d) 1% (expressed as Cu) Cu-en

e) 1% (expressed as Cu) Cu-DAP

f) 1% (expressed as Cu) Cu-AEEA

g) 1% (expressed as Cu) Cu-Polyim

8.2.4. Reactions of chrysin and taxifolin with ammoniacal copper/copper-amine solutions

To determine the composition of the reaction products of chrysin and ammoniacal copper solution, 0.0254 g chrysin was dissolved in 100 ml of methanol and reacted with 0.005 M ammoniacal copper sulphate solution. The reactions between Cu-MEA, Cu-en, and Cu-AEEA and chrysin were also studied to identify whether a similar reaction would occur. In this case, 0.01 mol in 100 ml chrysin-methanol solution was reacted with 0.005 mol copper amine solution.

The reactions of taxifolin and copper-amine solutions were investigated to determine whether a similar black reaction takes place, as reported earlier for the

ammoniacal copper solution. Copper monoethanolamine and copper ethylenediamine were selected to represent ethanolamine and diamine systems, respectively. Copper-HDO ethylenediamine solution was used to investigate the reaction when HDO was present. A 15 ml aliquot of a 1 % copper-amine or CuHDO-en solution was added to 1.0 mmol (304.0 mg) of the purified taxifolin dissolved in anhydrous methanol (20 ml). After two hours taxifolin was no longer detected during TLC analysis. It indicated that almost all taxifolin reacted with copper ions.

The precipitates formed during the reactions were filtered, washed three times with distilled water, and air-dried. The FTIR spectra of the precipitate prepared as a KBr pellet were recorded on a Perkin-Elmer 1600™ spectrophotometer with 4 scans, at a resolution of 4 cm^{-1}, over the range of 400-4000 cm^{-1}. The precipitates formed during reactions with chrysin or taxifolin were dissolved in DMSO solution for ESR measurement at 150 K. The precipitate was also prepared as a compressed pellet for XPS examination. Elemental analysis of the precipitates for carbon, nitrogen, and copper was carried out by the Canadian Microanalysis Company, Ladner, B. C. to confirm their composition.

8.3. Results and discussion

8.3.1. Preliminary reaction of Scots pine and Douglas-fir extractives with basic copper solutions

Reactions of Scots pine and Douglas-fir extractives with different copper solutions were observed. The results are shown in Table 8-1. Copper sulphate solution alone did not produce any precipitate with either extractive solution. However, copious dark-brown precipitates were observed in reactions with ammoniacal copper sulphate solution. This confirmed the earlier findings of a dark colored precipitation reaction between Douglas-fir heartwood and ammoniacal copper solution (Ruddick and Xie, 1994). The copper monoamine systems (Cu-MEA and Cu-Polyim) showed a promising reaction with both Scots pine extractives and Douglas-fir extractives. A large amount of green precipitate was formed with each extractive methanol solution. The reactions of Douglas-fir extractive solution with copper diamines (Cu-en, Cu-DAP, and Cu-AEEA) produced small amounts of brown precipitates, while only the reaction of Scots pine extractive solution with Cu-AEEA formed a solid. No precipitate was observed during reaction of Scots pine extractive solution and Cu-en or Cu-DAP solutions, reflecting the low reactivity of the copper diamine solutions with Scots pine and Douglas-fir heartwood extractives, compared to that of copper monoethanolamine.

Table 8-1. Reaction products of Scots pine and Douglas-fir extractive solutions with copper solutions.

	$CuSO_4$	$CuSO_4$ + NH_4OH	Cu-MEA	Cu-en	Cu-DAP	Cu-AEEA	Cu-Polyim
Scots pine Extractives	No PP*	Brown PP+**	Green PP+	No PP	No PP	Brown PP	Green PP+
Douglas-fir Extractives	No PP	Brown PP+	Green PP+	Brown PP	Brown PP	Brown PP	Green PP+

* PP: precipitate
** PP+: extensive precipitation

8.3.2. Reactions of ammoniacal copper sulphate and copper-amine solutions (Cu-MEA, Cu-en, and Cu-AEEA) with chrysin

In flavonones, copper can be chelated by either the 3-hydroxyl and 4-keto, or 5-hydroxy and 4-keto groups, forming a 6-membered or 5-membered ring (Figure 8-2) (Jurd, 1962; Sakamato and Takamura, 1978; Takamura and Sakamato, 1978). In taxifolin the reactivity of the proton on the 5-hydroxyl group conjugated with benzene ring A, is greater than that on the 3-hydroxyl group, so that copper chelation to the A ring is anticipated. This reactivity of the 5-hydroxyl group was confirmed by Porter and Markham (1972) who demonstrated that metal ions were preferentially chelated at this position in dihydroflavonols. Following complex formation involving the 5-hydroxyl and the ketone groups, further reaction with the 3-hydroxyl group on ring A can be eliminated. Further coordination is possible through the 3' and 4' hydroxyl groups on ring B of taxifolin (Figure 8-2). The 3-hydroxyl is either not involved in reaction

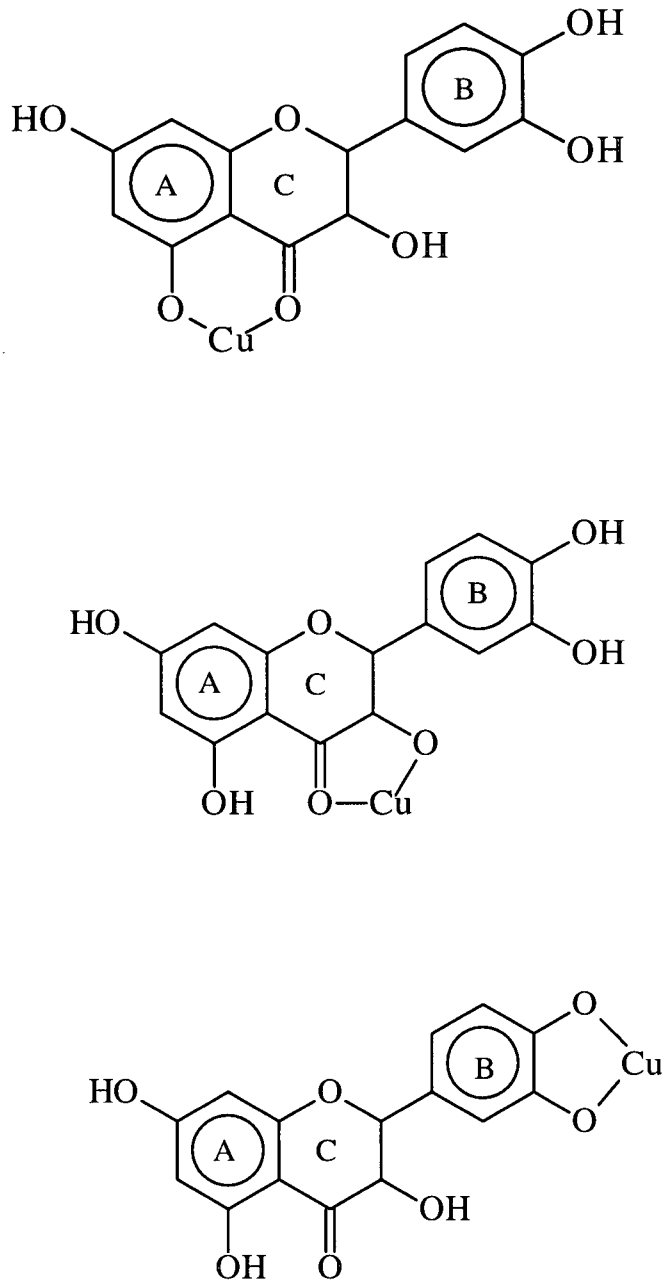


Figure 8-2. Potential reaction sites for copper in taxifolin.

with copper. It was reported by Ruddick and Xie (1994) that the black precipitate formed had the composition $[Taxifolin]_2.Cu_3.(NH_3)_4.2H_2O$. It was proposed that the ammonia was bonded to the copper which chelated with the 3' and 4' hydroxyl groups on the B ring. In order to provide further information, the reaction of chrysin and ammoniacal copper sulphate solution was investigated.

A green precipitate resulted from the reaction of chrysin and ammoniacal copper sulphate. The FTIR spectra of chrysin and the green solid formed during the reaction are shown in Figure 8-3.

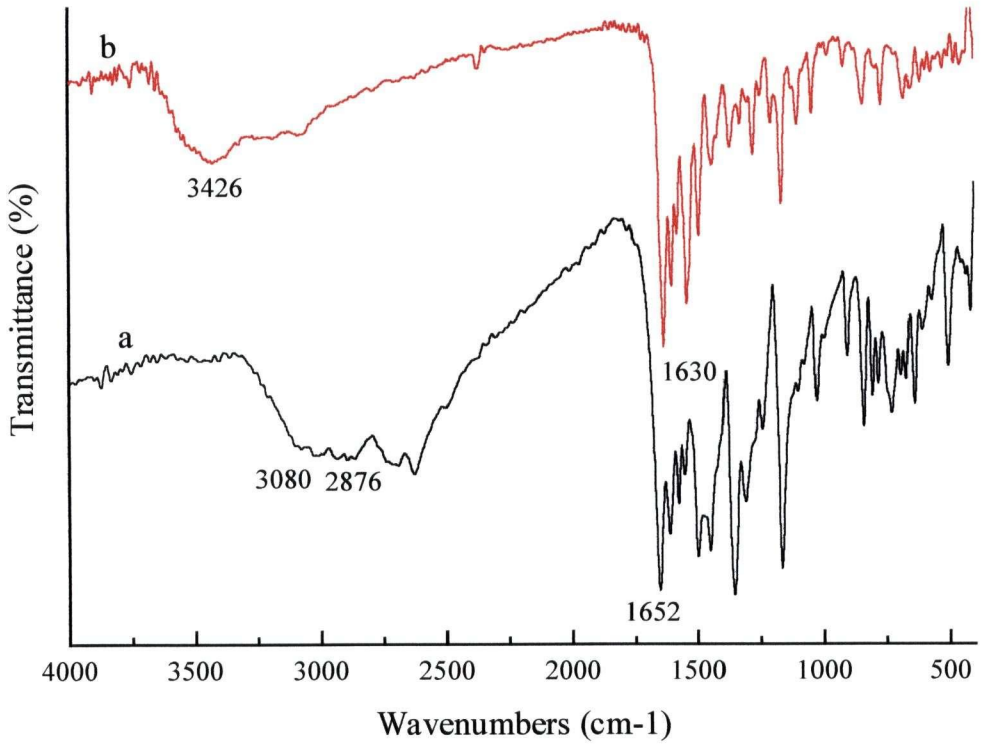


Figure 8-3. FTIR spectra of a) chrysin, and b) the green precipitate formed during the reaction of chrysin and ammoniacal copper solution.

It was established that the H-bonded -OH occurred at 3600-2500 cm^{-1} as a broad peak, and at the lower frequency, the stronger the H-bond (Williams and Fleming, 1966). The O-H stretching vibration in chrysin appeared at the absorption region of 2876-3080 cm^{-1}. The lower band is due to intra-molecular H-bond and the higher band is arisen from inter-molecular H-bond for free chrysin. After reacting with ammoniacal copper solution, this region was shifted to 3426 cm^{-1}, suggesting that the hydroxyl and ketone groups in ring A are involved in chelate formation with copper. This resulted in the loss of intra-molecular H-bond between ring A and ring C, and the replacement of inter-molecular H-bond -OH in ring A, after loss of the chelation site at ring A and C by the reaction with copper. The peak at 1652 cm^{-1}, due to the ketone bonding in chrysin, was shifted to 1630 cm^{-1} in the green solid, confirming the involvement of this group during complex formation. However, it is not clear from the FTIR spectrum whether ammonia is present in the green precipitate.

The green copper complex dissolved sufficiently in DMSO so that an ESR spectrum was observable at 150 K. It is shown in Figure 8-4 that the values of $g_{//}$ and $A_{//}$ were 2.36 and 138 respectively. They are typical for copper bound to four oxygen atoms, confirming that ammonia was not present in the green copper complex. The elemental analytical results of this green solid recorded less than 0.1% nitrogen, confirming that no ammonia remained in the copper chrysin product.

Based on the ESR and FTIR data, it is suggested that copper is bonded via the hydroxyl and ketone groups, and the ratio of copper to chrysin could be 1:2. Any reaction, involving the 3' and 4' hydroxyl groups on ring B in taxifolin, is eliminated. The

nature of the compound formed, together with the chemical analysis confirmed that no copper-nitrogen compounds were present in the copper-chrysin complex.

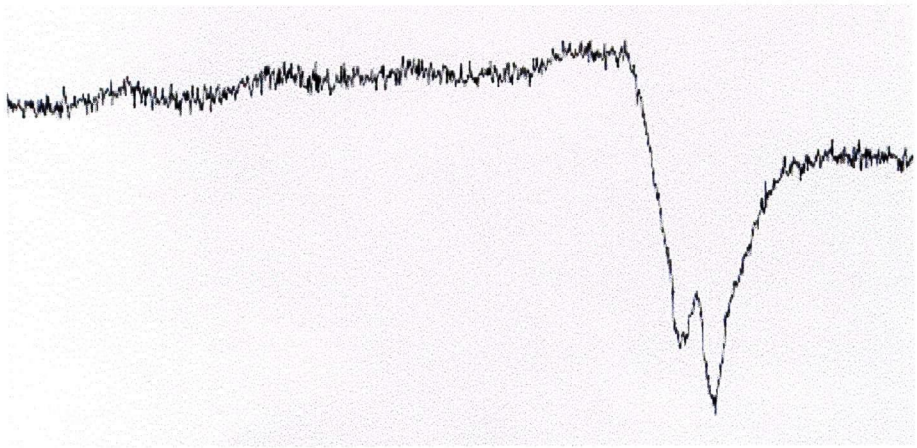


Figure 8-4. ESR spectrum of green solid from the reaction of chrysin and ammoniacal copper sulphate.

Green precipitates were produced during reaction of chrysin and Cu-MEA, while brown precipitates resulted from reaction of chrysin with Cu-en and Cu-AEEA. The precipitates were characterized by FTIR, XPS, and ESR analysis. The FTIR spectra of Cu-MEA, Cu-en, and Cu-AEEA treated chrysin are shown in Figure 8-5. Similar to the observations found in ammoniacal copper sulphate treated chrysin, the two changes in the FTIR spectrum are the shifts of the O-H stretching vibration (from 2876-3080 cm^{-1} in chrysin to 3250-3410 cm^{-1} in copper-amine treated chrysin), and the ketone C=O stretching vibration (from 1652 cm^{-1} to 1630 cm^{-1}). These observations suggest that the hydroxyl group and ketone group on chrysin are responsible for the chelate formation of copper during the reaction. The presence of nitrogen in the copper complexes could not be confirmed by the FTIR measurement.

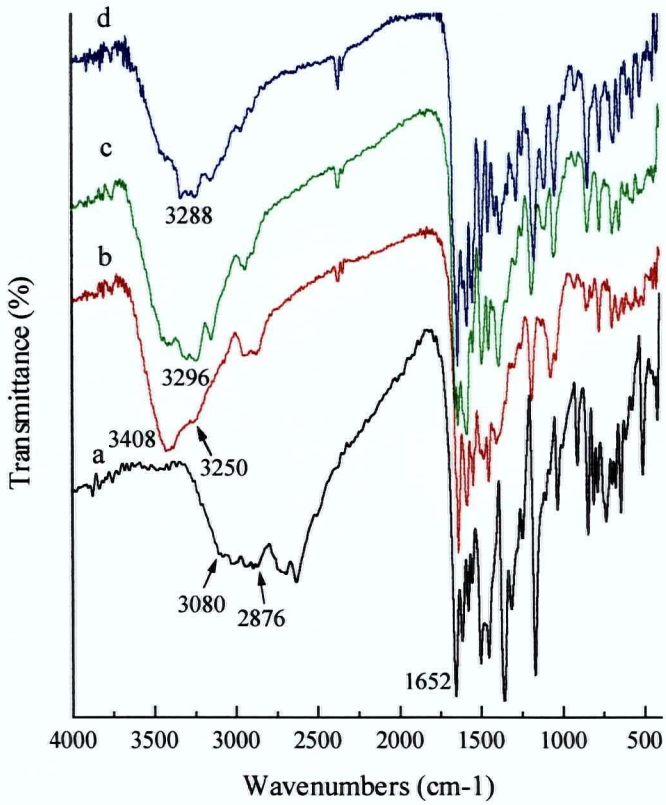


Figure 8-5. FTIR spectra of a) chrysin, b) Cu-MEA treated chrysin, c) Cu-en treated chrysin, and d) Cu-AEEA treated chrysin.

During XPS analysis, one nitrogen peak was observed in the N1s XPS spectra of copper amine treated chrysin, with a binding energy at 399.71 eV for Cu-MEA, 399.88 eV for Cu-en, and 399.66 eV for Cu-AEEA (Table 8-2). The binding energies are consistent with those observed for the copper-amine complex with the phenolic hydroxyl group in wood.

ESR analysis provided further information on how the nitrogen is coordinated to copper in the products of chrysin and copper-amine. The values of $g_{//}$ and $A_{//}$ are 2.24 and 188, respectively, for the brown copper complex formed from the reaction of chrysin and Cu-en, although no hyperfine was visible in the ESR spectra of Cu-MEA and Cu-AEEA treated chrysin (Table 8-3). The values of $g_{//}$ and $A_{//}$ compared well with those assigned to copper complexed to four nitrogen atoms in a planar structure, implying that one mole of copper is coordinated to two moles of amine in the copper-chrysin complex.

Table 8-2. The binding energies of N1s and Cu2p spectra for copper-amine or copper-HDO ethylenediamine treated chrysin and taxifolin.

Sample ID	N1s (eV)	Cu2p (eV)	
		Cu1	Cu2
Chrysin-CuMEA	399.71	932.92	934.78
Chrysin-Cuen	399.88	933.25	934.80
Chrysin-CuAEEA	399.66	932.25	934.30
Taxifolin-CuMEA	399.97	932.69	934.38
Taxifolin-Cuen	399.51	932.70	934.31
Taxifolin-CuHDOen	399.78	932.84	934.22

Table 8-3. ESR spectral parameters of $g_{//}$ and $A_{//}$ for copper-amine or copper-HDO ethylenediamine treated chrysin and taxifolin.

Sample ID	$g_{//}$	$A_{//}$
Chrysin-CuMEA	--*	--
Chrysin-Cuen	2.24	188
Chrysin-CuAEEA	--	--
Taxifolin-CuMEA	2.27	173
Taxifolin-Cuen	2.24	187
Taxifolin-CuHDOen	2.24	188

* No hyperfine structure

8.3.3. Reactions of taxifolin from Douglas-fir and Cu-MEA, Cu-en, and CuHDO-en solutions

The structure of taxifolin is shown in Figure 8-1. Taxifolin is a major phenolic extractive in Douglas-fir, being first isolated by Pew in 1948. The average concentration of taxifolin in Douglas-fir was found to be 1%. Taxifolin is quite soluble in hot water (13.5% at 100 °C) and relatively insoluble in cold water (0.25% at 25 °C).

A green precipitate was formed immediately when copper monoethanolamine solution was mixed with a taxifolin-methanol solution. Dark brown precipitates were produced during the reaction of Cu-en and Cu-AEEA with taxifolin. The FTIR spectra of the taxifolin and the reaction products formed with Cu-MEA, Cu-en, and CuHDO-en are shown in Figure 8-6. The FTIR spectrum of taxifolin contains several characteristic peaks, which were identified in Table 8-4 (Ruddick and Xie, 1994). The peaks at 3550 cm^{-1} and 3400 cm^{-1} are related to the O-H stretching vibration. After the reaction, the peak at 3550 cm^{-1} disappeared, and the peak at 3400 cm^{-1} broadened and decreased. The

absorption at 1630 cm^{-1} associated with the ketone carbonyl stretching vibration in taxifolin was shifted to 1605 cm^{-1} for Cu-MEA treatment, and to 1615 cm^{-1} for Cu-en and CuHDO-en treatments. The intensity of the peak at 1364 cm^{-1} due to the O-H in plane bending vibration, was reduced for all the treatments. These observations confirm the involvement of the hydroxyl and ketone groups during copper complex formation in all three precipitates.

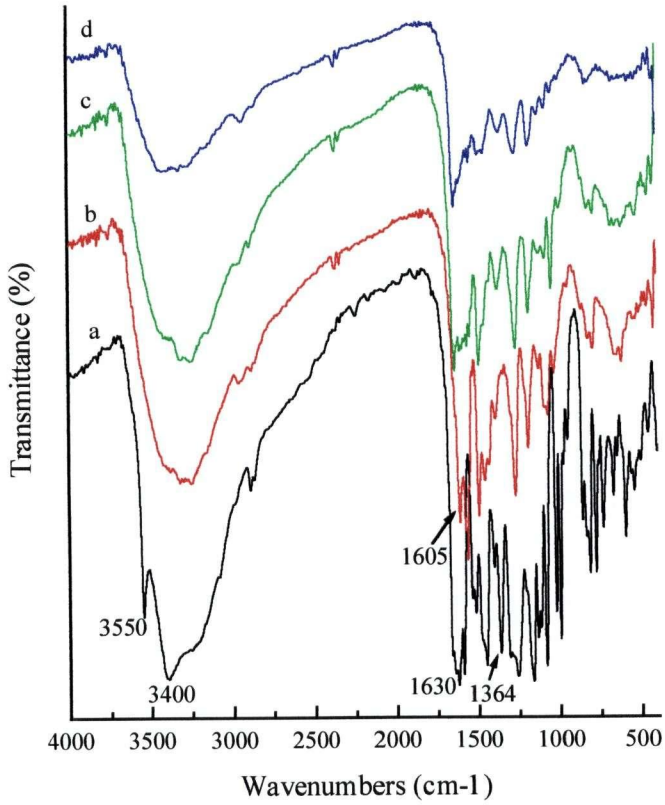


Figure 8-6. FTIR spectra of a) taxifolin, b) Cu-MEA treated taxifolin, c) Cu-en treated taxifolin, and d) CuHDO-en treated taxifolin.

Table 8-4. Assignment of absorption bands in the infrared spectrum of taxifolin.

Wavenumbers (cm-1)	Assignment
3400-3500	O-H stretching vibration
1630-1640	C=O stretching vibration
1430-1510	C-H bending vibration/aromatic skeletal vibration
1359-1390	O-H in plane bending vibration
1000-1250	C-O-C stretching vibration
973	-CH out of plane deformation
750-875	C-H out of plane bending vibration
680	C-C out of plane bending vibration

In XPS measurements, the nitrogen peak of Cu-MEA, Cu-en, and CuHDO-en treated taxifolin displayed very consistent results. Only one nitrogen peak was found for all treatments. The binding energy of the nitrogen was located around 400 eV (Table 8-2). This is the binding energy previously assigned to the nitrogen in the copper-amine complex in wood. No characteristic binding energy for nitrogen in $Cu(HDO)_2$ precipitate was observed in the CuHDO-en treated taxifolin. It may be concluded, therefore, that $Cu(HDO)_2$ is not formed during the reaction with taxifolin. The copper binding energy for the reaction product formed from CuHDO-en and taxifolin is 934.3 eV (Table 8-2). This is too low for the binding energy of copper in $Cu(HDO)_2$ (935.86 eV), further confirming that $Cu(HDO)_2$ is not formed during the reaction.

ESR analysis provided additional information on how the nitrogen is coordinated to copper in the copper-amine complex formed with taxifolin. Only one copper species was observed in the ESR spectra of Cu-MEA, Cu-en, and CuHDO-en treated taxifolin.

As shown in Table 8-3, the copper complex produced from the reaction of taxifolin and Cu-MEA showed a value of $g_{//}$ at 2.27, and $A_{//}$ at 173. The ESR parameters are in good agreement with those of copper bound to two nitrogen atoms, suggesting one mole of copper is complexed to two moles of amine in the copper ethanolamine complex formed with taxifolin. The reactions of Cu-en and CuHDO-en with taxifolin gave similar ESR parameters with a lower $g_{//}$ value, but higher $A_{//}$ value, reflecting the similar coordination environment of copper in the copper complex formed during the reactions with taxifolin. The values of $g_{//}$ and $A_{//}$ are consistent with those observed for copper complexes formed with organosolv lignin having four equatorial copper-nitrogen donor bonds. This suggests that the copper-taxifolin complex appears to have the same configuration as copper in the corresponding copper-amine organolslov lignin, in which four copper-nitrogen equatorial bonds form a plane. The chelation mechanism involved is similar. It is expected that under the highly alkaline condition, the phenolic hydroxyl groups in taxifolin are readily deprotonated, and copper is easily chelated to the hydroxyl group and the adjacent ketone group.

8.4. Conclusions

1. Extractives from Scots pine heartwood and Douglas-fir heartwood reacted readily with Cu-MEA and Cu-Polyim to produce green precipitates. The diamine-copper system (Cu-en, Cu-DAP, and Cu-AEEA) showed much lower reactivity with the same extractives.
2. A green precipitate was formed during the reaction of chrysin and ammoniacal copper sulphate. The copper-chrysin complex did not contain any nitrogen. ESR measurement suggested that the ratio of copper to chrysin in the copper-chrysin complex is 1:2. It is postulated that in taxifolin, the most likely position for copper bound with ammonia is on the 3' and 4' hydroxyl groups.
3. The reaction of chrysin and Cu-MEA produced a green precipitate, while a brown precipitate was formed during the reactions of chrysin and Cu-en and Cu-AEEA. FTIR spectra of the formed copper complexes suggested that the hydroxyl group and ketone group are the major sites for copper chelation. XPS and ESR analyses confirmed the presence of nitrogen, and suggested that one mole copper is coordinated to two moles of amine in the copper-amine complexes formed with chrysin.
4. A green precipitate was produced in the reaction of taxifolin and Cu-MEA, while brown precipitates were formed in the reactions of taxifolin and Cu-en and CuHDO-en. It was found that amine remained in the copper-taxifolin complexes as shown by XPS, and ESR provided further information that the central copper is coordinated with two amines in the copper-taxifolin complexes. No evidence supported the

formation of $Cu(HDO)_2$ precipitate during the reaction of taxifolin and CuHDO-en. The hydroxyl groups and ketone group were considered the major positions responsible for the copper chelation.

Chapter 9

Studies on the distribution of copper element and $Cu(HDO)_2$ precipitate in wood

9.1. Introduction

The location and distribution of copper preservative components in wood are related primarily to wood ultrastructure, density, and the fixation reaction between wood components and the copper solution. Different fixation mechanisms of copper are expected to give rise to different distribution patterns. Reaction of copper with wood components, such as lignin or extractives, will cause copper to locate where high concentrations of these reactants are found (i.e. in the cell corner or resin canal respectively). On the other hand, if the simple precipitation of copper is the major fixation reaction, copper will be found mostly on the lumen surface. Generally, low density of wood species would allow preservative solution to flow easily into wood, resulting in good distribution. The type, number, and size of pits in the wood would directly influence the penetration of preservative (Brennan et. al., 1995; DeGroot and Kuster, 1986).

The two most commonly used methods to determine the distribution of chemicals in wood are visible microscopy and scanning electron microscopy coupled with energy dispersive x-ray analysis (SEM-EDX). Visible microscopy can provide direct observation of the chemical location in thin sections after metal specific staining, when the chemicals are well fixed in wood, and a suitable staining reagent is applied. In 1959, Belford and

co-workers examined Douglas-fir sapwood, treated with CCA. They found that sections stained with dithio-oxamide showed a strong response at the middle lamella, with a weaker blue color in the cell wall. Resch and Arganbrigth (1971) reported the distribution of pentachlorophenol in Douglas-fir using dimethylanilin. They noted an enhanced reaction with the epithelial cells associated with the resin canals and tracheids. One of the most extensive visible microscopic studies of chemically treated wood was carried out by Yata et. al. (1979 and 1981). They examined the distribution of several metals, including copper and zinc.

SEM-EDX is also well established as a useful tool to study the micro-distribution of chemicals in wood. SEM-EDX is capable of observing and identifying any metal precipitate formed, and provides semi-quantitative information on elemental distribution in wood. There are many reports of the micro-distribution of CCA in wood (Greaves, 1972 & 1974; Greaves & Levy, 1978; and DeGroot & Kuster, 1986). It is recognized that results obtained using this technique are only semi-quantitative even under optimum conditions (Hall and Hohling, 1968). Yata et. al. (1983) examined the influence of the electron beam surface area, as well as the penetration by the beam into the wood surface. Both are critical in defining the amount of wood analyzed. Since wood density varies from cell to cell, the beam penetration will also change between cells. Quantification of the x-ray emitted by a sample is only possible for thin sections, since both matrix effects and interference by other elements can affect the x-ray counts detected. In addition, wood is very heterogeneous, and x-ray results for even the same cell type and location in the cell may vary widely; so it is important to provide an indication of the range of values

observed. A significant advantage of SEM-EDX is to clearly detect and identify the components present in precipitates in wood (Craciun et. al., 1997).

However, SEM-EDX analysis is subject to errors. For example, the re-distribution of chemical may occur during sample preparation (Ryan, 1986). In addition, x-rays may be generated by adjacent regions but be detected during analysis, thus SEM-EDX bulk measurements may not reflect the amount of chemical at a specific location (Yata et. al., 1983). Consequently, the SEM-EDX data will show some variability, so that many measurements must be made, if overall trends in distribution of chemical in different cell types are to be developed.

The main objective of this research component was to seek evidence to support the hypothesis that during treatment of wood with copper-HDO amine, a precipitate of $Cu(HDO)_2$ is preferentially formed. Useful information would also be gained on the distribution and location of copper in copper amine and copper-HDO amine treated wood using light microscopy and SEM-EDX.

9.2. Materials and methods

9.2.1. Light microscopy

Southern pine and Douglas-fir sapwood blocks (50 x15 x 15mm) were soaked in CuMEA or CuHDO-en solution (1% CuO) for three hours. Afterwards, the blocks were removed from the treating solutions and air-dried for two weeks at room temperature, to ensure the completion of fixation. Thin sections were prepared from Cu-MEA and CuHDO-en treated southern pine and Douglas-fir sapwood blocks for light microscopy. All cutting and microtoming was performed on dry samples to minimize the redistribution or loss of chemical. The treated blocks were mounted on a Spencer™ sliding microtome. The sample surface was covered with a thin layer of distilled water and then microtomed to produce 18 μm thick thin sections. The thin sections were immediately removed and placed overnight in the previously prepared 0.2 % dithio-oxamide ethanol staining solution. The cells containing copper (Cu^{2+}) were stained dark green, while untreated cells retained their original color. After staining, the thin sections were removed and dehydrated by washing with ethanol until the wash-ethanol was free of color. The thin sections were then kept in 1:1 ethanol and glycerin solution for 10 minutes, after which they were soaked in pure glycerin for another 10 minutes. Each thin section was mounted between a microscopic glass slide and glass cover for later observation by light microscopy.

The stained thin sections were examined using a Jenamed 2 (Carl Zeiss™) light microscope fitted with a Pentacon™ camera. Representative samples were photographed using 135 Fuji 100 film.

9.2.2. SEM-EDX

9.2.2.1. Sample preparation

Cu-MEA, Cu-en, and CuHDO-en treated Scots pine sapwood blocks, which had previously been either unleached or leached with distilled water, were selected. Their treatment and leaching has been described previously (Section 3.2). Sample preparation for SEM-EDX analysis is critical, since it can directly influence the measured chemical distribution. Care was taken to ensure that the sample surface was as clean and smooth as possible, by using fresh microtome blades, and removing a number of thin sections prior to collecting sections for analysis. The sample moisture content was maintained below 10% to minimize chemical movement and loss.

All samples were removed from the outer 5 mm of the treated blocks. The surfaces of the samples were smoothed using a Spencer sliding microtome. Cross, radial, and tangential sections (5mm x 5mm by 2mm in thickness) were cut from the smoothed surface of each block. The samples were attached with the smooth surface upper most on to aluminum stubs using double-sided tape. They were then coated with carbon (thickness of 300-400 Å) using a vacuum thermal evaporator.

9.2.2.2. SEM-EDX examination

A Hitachi S-570 Scanning Electron Microscopy™ (SEM) coupled with a Kevex 8000 Energy Dispersive X-ray™ analyzer (EDX) was used for the analysis of the copper micro-distribution. The operating conditions were a 20 kV accelerating voltage and a 23 mm working distance. Each analysis duration was 175 seconds. Measurements were made on latewood tracheid cell walls, compound middle lamelle, and ray cell walls. Six analyses per location within each sample were collected and the results averaged. X-ray counts of copper were converted into corrected peak to background ratio (peak area) using the following equation:

$$\mathrm{R} = \frac{P - B}{B}$$

Where: R: corrected peak to background ratio (peak area)

P: X-ray peak count

B: X-ray background count.

Care was taken when selecting the analysis locations, because the copper content will depend upon the cell type and anatomical feature, being examined. To reduce the data variation and to increase comparability between treatments, the analysis locations were chosen in the different samples to be as similar as possible. Spot analyses at the compound middle lamella (CML) and secondary wall region (SS) within selected tracheids, were also carried out (Figure 9-1). The absolute magnitude of the copper peak to background ratio is influenced by many factors, including x-ray beam intensity, copper content in the wood, wood density at the analytical region, and the presence of surface

deposits in cell pits, resin canals or cell lumens. Consequently, variation in the copper content is to be expected.

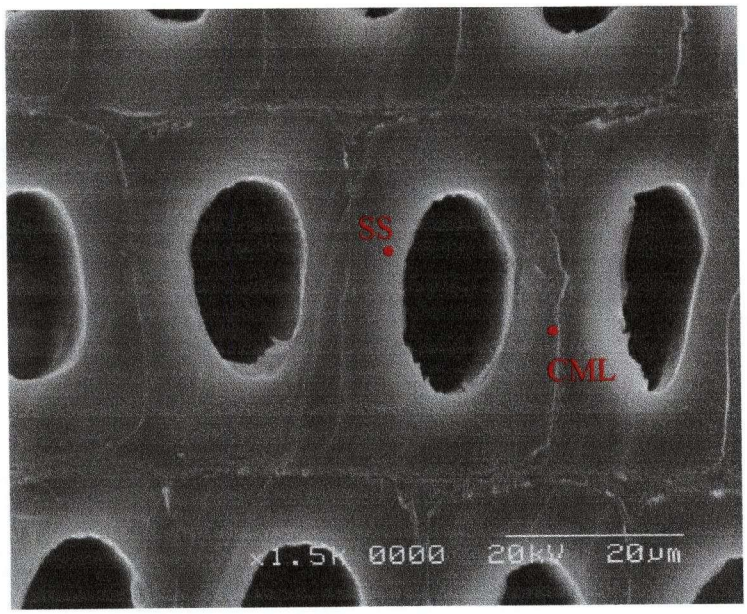


Figure 9-1. Typical tracheid cell walls showing the compound middle lamella (CML) and secondary wall (SS) regions.

9.3. Results and discussion

9.3.1. Light microscopy

The appearance of copper amine treated wood sections under light microscopy, after staining with dithio-oxamide to observe the copper distribution, is very revealing (Figure 9-2 to 9-5).

For both wood species, there is little evidence of copper being deposit on the tracheid lumen surface. The green color due to copper reaction with dithio-oxamide could be observed throughout the cell wall but was particularly pronounced in the compound middle lamella (CML) and cell corners (CC) (Figure 9-2 and 9-4). This observation of a high copper concentration in the compound middle lamella and cell corners has been reported for CCA treated wood by several researchers (Greaves, 1972 and 1974; An et. al., 1998; Belford et. al., 1959). This is consistent with the earlier studies of the fixation chemistry described in Chapters 4 and 6, in which copper-lignin reactions were found to be one of the main fixation reactions, since the middle lamella and the cell corner in particular are highly lignified areas, with the latter reaching almost 85% (Sjostrom, 1993). The importance of copper reactions with the guaiacal groups of lignin was also directly identified during the earlier studies of copper-amine-vanillin model reactions (Chapter 5).

The ray cells were heavily stained dark green for both wood species. This confirms the known importance of the ray cell (R) in transporting the copper-amine solution into wood (Figure 9-2 to 9-5) (An et. al., 1998). The semi-bordered pit pairs adjacent to the ray cell were deeply stained, supporting their role in transferring copper-

amine solution from the ray cell into the adjacent tracheids. The intensity of the copper reaction was strong even several cells distance from the ray cell, suggesting the excellent penetrating characteristics of the copper amine solution.

Resin canals have been shown to also contribute to CCA preservative solution movement in wood (An et. al. 1998, and An, 1999). It may be expected that copper amine solutions would behave similarly. Both transverse and longitudinal resin canals were found to be stained more heavily than the surrounding tracheids (RC in Figures 9-2 and 9-5). The precipitation of copper compounds in the resin canals would be anticipated from the reported reaction of ammoniacal copper solution with wood extractives, such as resin and fatty acids (pine), taxifolin (Douglas-fir), to form very stable copper complexes (Ruddick and Xie, 1994). The formation of crystalline solids in the resin canals and associated epithelial cells has been reported previously (An, 1999 and Ruddick, 1978).

The copper distribution in copper-HDO ethylenediamine treated wood is shown in Figure 9-6 to 9-9. Comparing these sections with those of copper-amine treated wood, the striking difference in the former is that copper is mostly deposited on the tracheid lumen surfaces, rather than in the highly lignified compound middle lamella and cell corners (Figure 9-6 and 9-8). Also, there appear to be greater deposits formed in the ray cells and resin canals. This is consistent with different fixation mechanisms for copper in copper-amine, and in copper-HDO amine treated wood, which was suggested earlier (Chapter 4). It was proposed in Chapter 4 that reactions between copper and carboxylic acid and phenolic hydroxyl protons in wood, are dominant in copper amine treated wood. For copper-HDO amine treatment, it is proposed that precipitation of $Cu(HDO)_2$ is favored, a

reaction which is driven by the decrease of pH in wood during fixation. The result of the light microscopy support this difference, with the $Cu(HDO)_2$ precipitate being clearly observed.

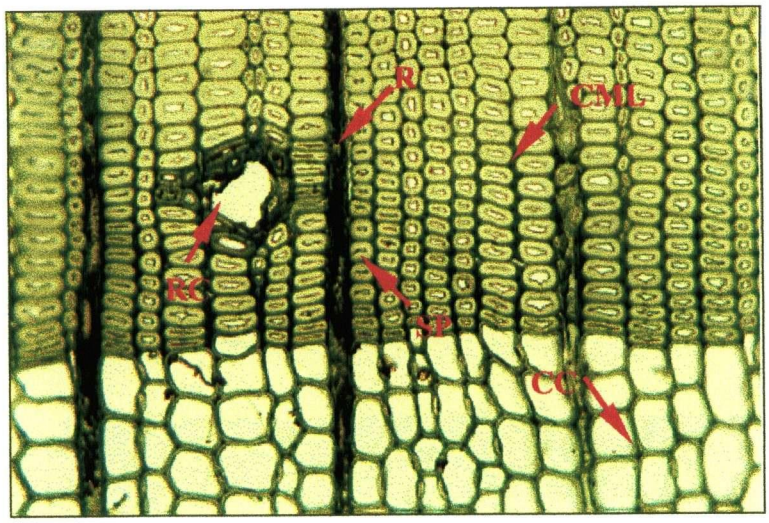


Figure 9-2. A micrograph of copper distribution in copper monoethanolamine treated southern pine sapwood (cross section). Magnification 50x. CC: cell corner. CML: compound middle lamella. RC: resin canal. R: ray cell. SP: semibordered pit pair.

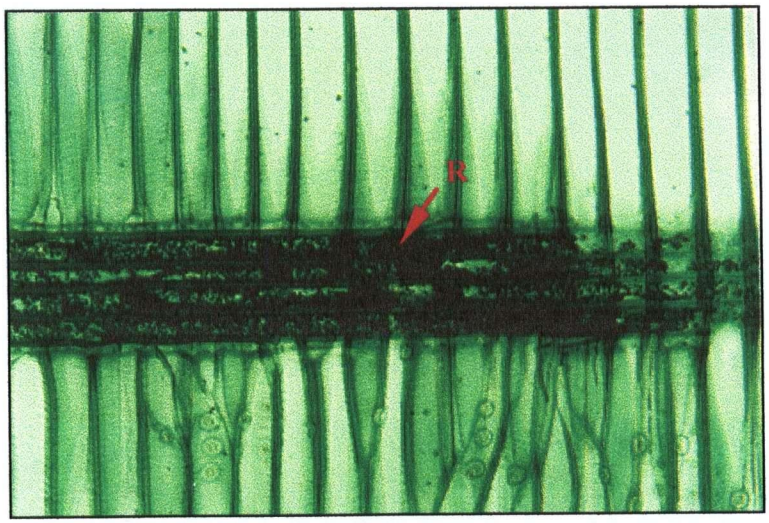


Figure 9-3. A micrograph of copper distribution in copper monoethanolamine treated southern pine sapwood (radial section). Magnification 50x. R: ray cell.

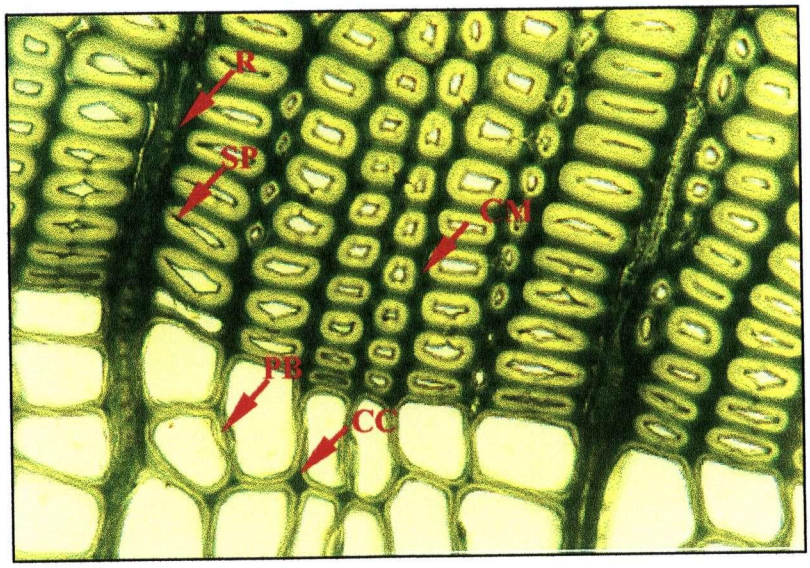


Figure 9-4. A micrograph of copper distribution in copper monoethanolamine treated Douglas-fir sapwood (cross section). Magnification 100x. CC: cell corner. CML: compound middle lamella. PB: bordered pit pair. R: ray cell. SP: semibordered pit pair.

Figure 9-5. A micrograph of copper distribution in copper monoethanolamine treated Douglas-fir sapwood (tangential section). Magnification 50x. RC: ray cell. RC: resin cell.

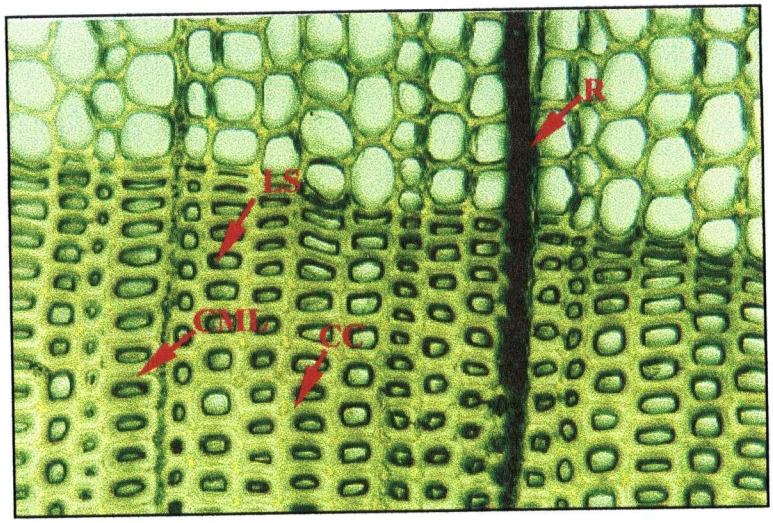


Figure 9-6. A micrograph of copper distribution in copper-HDO ethylenediamine treated southern pine sapwood (cross section). Magnification 50x. CC: cell corner. CML: compound middle lamella. R: ray cell. LS: lumen surface.

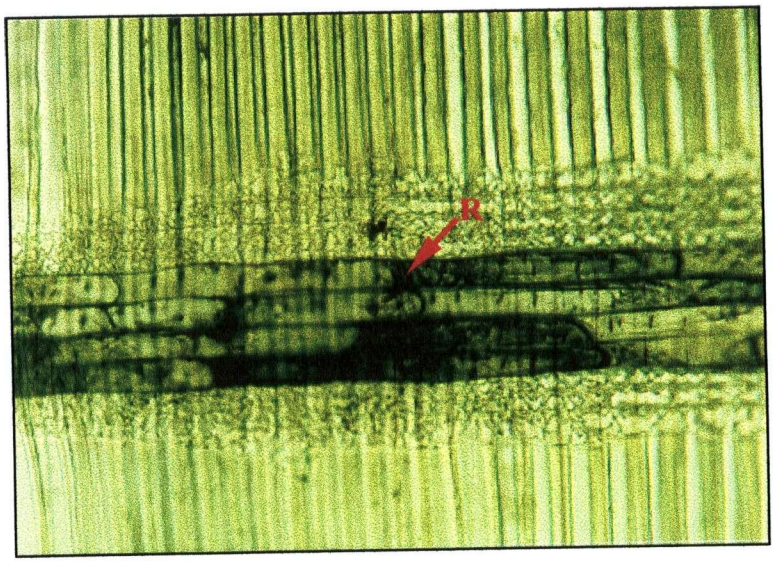


Figure 9-7. A micrograph of copper distribution in copper-HDO ethylenediamine treated southern pine sapwood (radial section). Magnification 50x. R: ray cell.

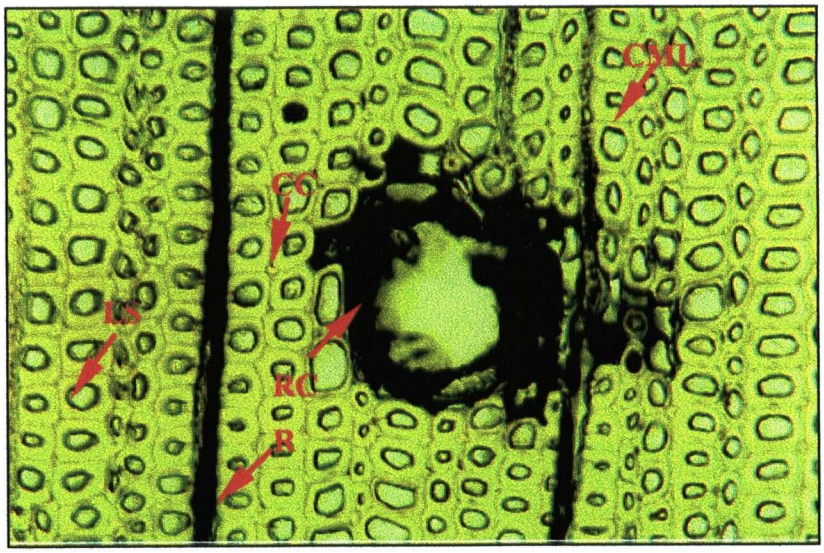


Figure 9-8. A micrograph of copper distribution in copper-HDO ethylenediamine treated Douglas-fir sapwood (cross section). Magnification 50x. CC: cell corner. CML: compound middle lamella. R: ray cell. RC: resin cell. LS: lumen surface.

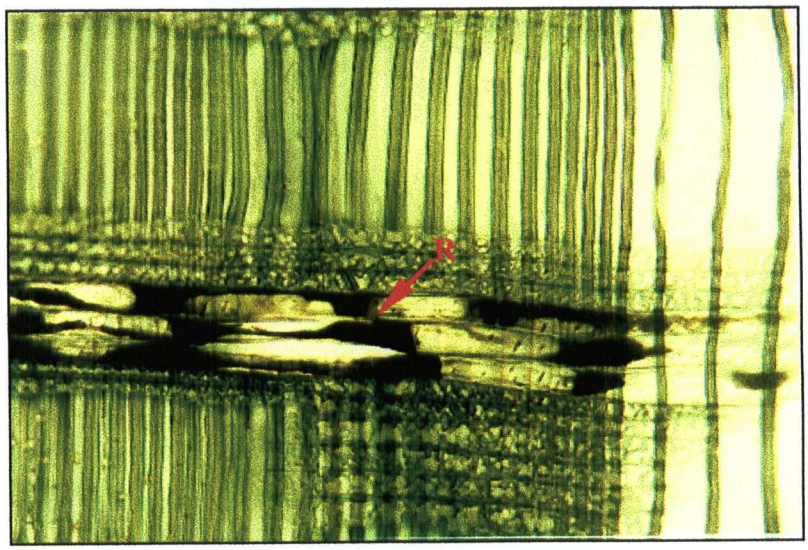


Figure 9-9. A micrograph of copper distribution in copper-HDO ethylenediamine treated Douglas-fir sapwood (radial section). Magnification 50x. R: ray cell.

9.3.2. SEM-EDX

Consistent with the visible microscopy observations, no deposits were noted in the copper-amine treated wood samples (Figure 9-10). However, in copper-HDO ethylenediamine treated wood samples, crystalline solids were observed in the tracheid lumens and pits (Figures 9-11 to 9-13). The copper peak area for the crystalline solids was extremely high. It is possible to demonstrate the high copper content of these deposits present on the cell wall by comparing copper dot-maps with the electron images of the crystalline solid distributions (Figure 9-11 to 9-13). This confirmed that the crystalline solid formed in wood contained high amounts of copper. Since no such precipitates were found in copper-amine treated samples, it is suggested that the solid formed resulted from a reaction between the copper and the HDO. This supports earlier spectroscopic evidence (Chapter 4), that $Cu(HDO)_2$ is preferentially formed in wood during reaction involving copper-HDO amine.

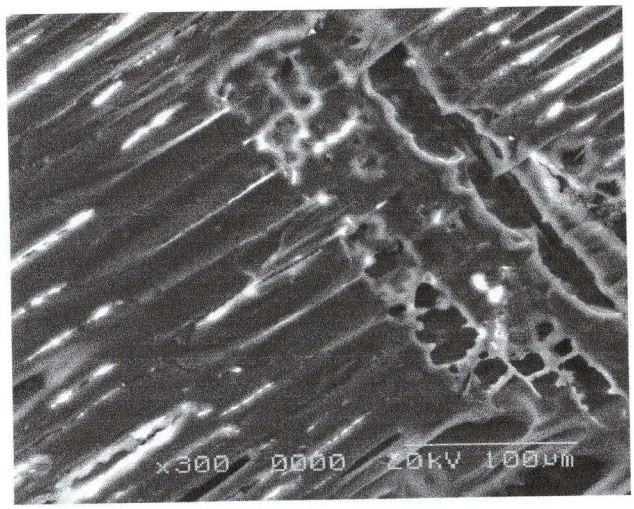
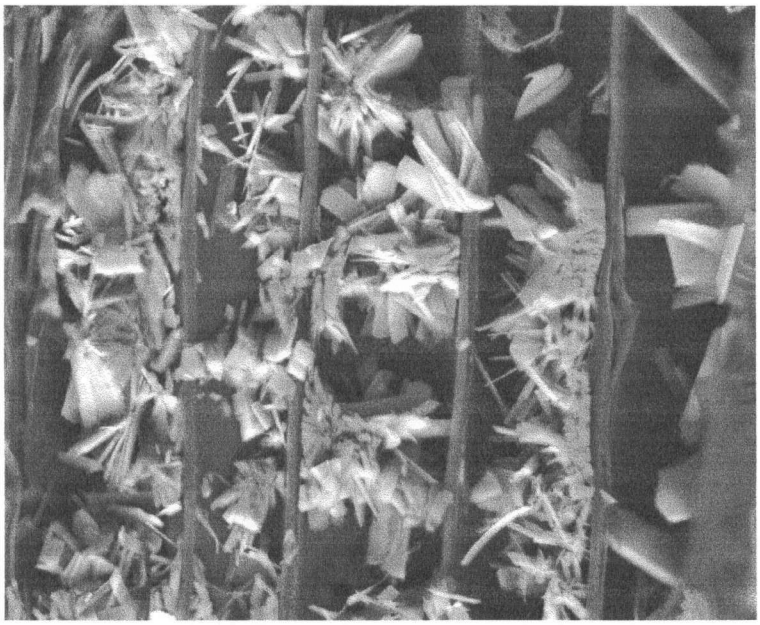
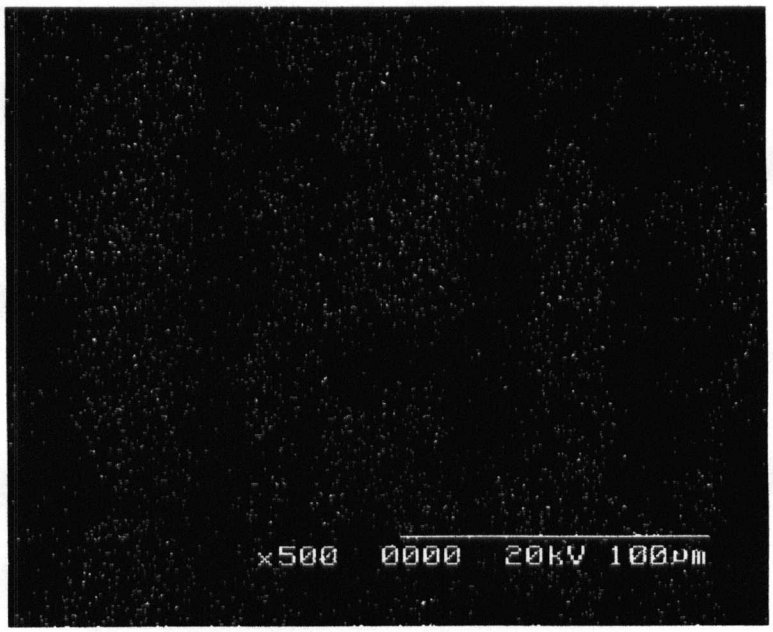


Figure 9-10. Scanning electron micrograph of copper ethylenediamine treated Scots pine (radial section).

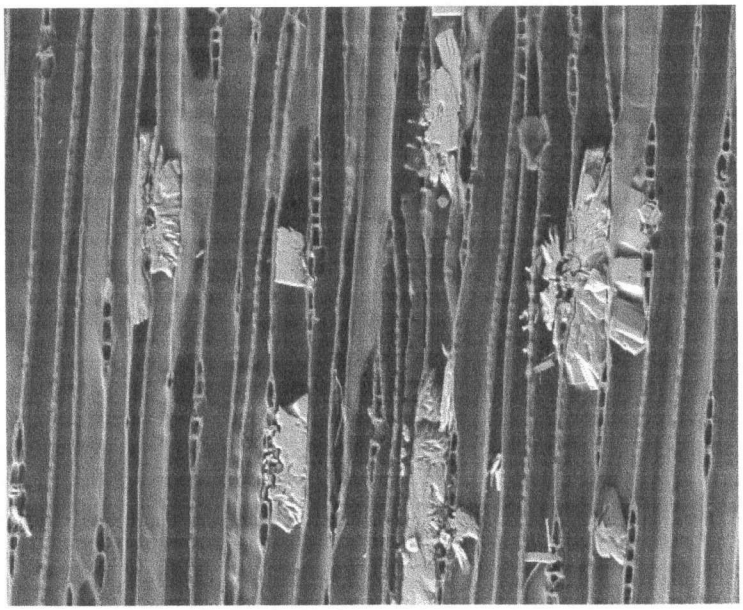


a



b

Figure 9-11. a) scanning electron micrograph and b) copper element map of copper-HDO ethylenediamine treated Scots pine (radial section).



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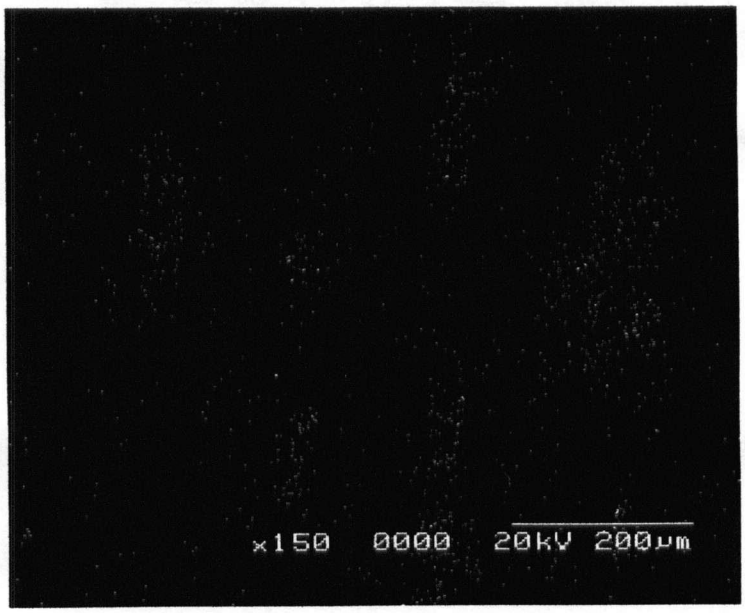
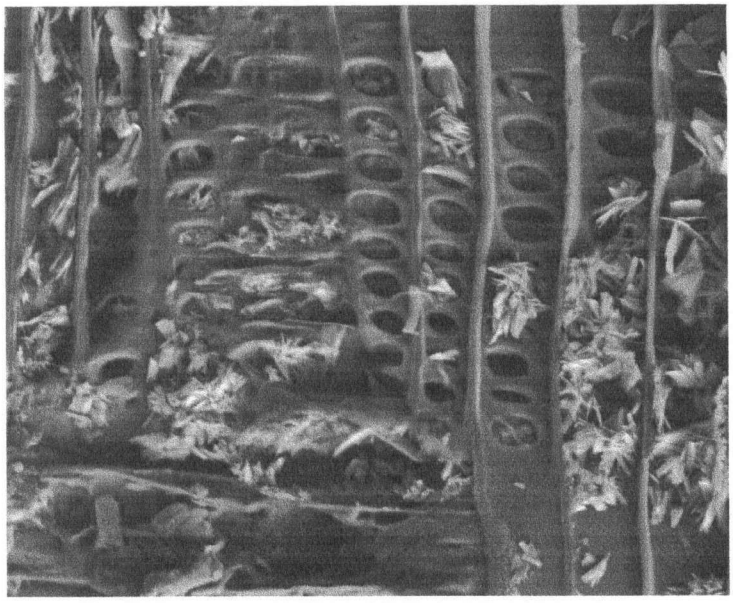
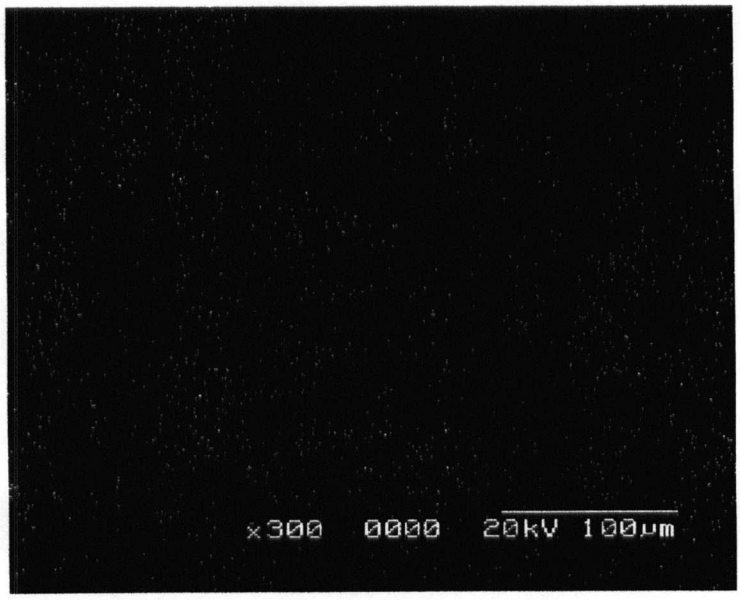


b

Figure 9-12. a) scanning electron micrograph and b) copper element map of copper-HDO ethylenediamine treated Scots pine (tangential section).



a



b

Figure 9-13. a) scanning electron micrograph and b) copper element map of copper-HDO ethylenediamine treated Scots pine (radial section).

The relative copper retentions in the latewood tracheid cell wall, compound middle lamella, and ray cell wall of Scots pine sapwood, are indicated by the corrected peak to background ratios presented in Table 9-1. Consistently, the copper in the ray cells is relatively high, confirming that this is one of the main avenues of solution penetration for copper-amine or copper-HDO amine solution and copper fixation. For copper-amine treatments, the copper distribution of Cu-MEA and Cu-en treated samples remained fairly constant in the different cell types.

In a pair testing of the observations, for both treatments, the greatest concentration of copper was found in the compound middle lamella. This is consistent with the observations from the light microscopy. However, the increase in corrected copper peak areas in the compound middle lamella area is not large. This is most probably due to the difficulty in analyzing only the middle lamella because of the minimum beam sampling area. Consequently, difference in the secondary wall and middle lamella values is reduced. After distilled water leaching, the copper concentration in Cu-en treated samples decreased dramatically compared to Cu-MEA treatment. This observation is consistent with the results of the leaching study of copper amine treated wood (Chapter 3), where Cu-MEA treated wood leached only 20% copper, whereas almost 50% of the copper in Cu-en treated wood was lost.

For copper-HDO amine treatment, the copper contents in the cell walls and compound middle lamella are much lower than the corresponding copper distribution in the copper amine treated samples. This again is in agreement with the results from light microscopy, where it was found that cell walls and the highly lignified areas of the

compound middle lamella and cell corners were not stained deeply for copper-HDO amine treated samples, indicating less copper was present at these locations. This low copper content (Table 9-1) implied that much less copper was available to react with wood components such as lignin and hemicellulose to form stable copper-wood complexes. The reason for this was that during reaction with the wood, $Cu(HDO)_2$ was preferentially depositing on the surface of the cell walls, particularly in the region of the pits (Figures 9-11 to 9-13).

Distilled water leaching did not significantly change the copper retention pattern for all three locations examined. The $Cu(HDO)_2$ is very immobile, as demonstrated from the water leaching study (Chapter 3).

Table 9-1. Peak to background ratios measured in Scots pine sapwood after treatment with copper-amine or copper-HDO amine solution.

Treatment	Latewood tracheid		Ray cell wall
	Cell wall	CML***	
Cu-MEA	6.126 (0.77**)	6.965 (1.08)	6.204 (0.55)
Cu-MEA-water*	4.004 (0.69)	4.948 (0.58)	4.352 (0.75)
Cu-en	6.425 (1.03)	6.946 (0.90)	6.719 (0.59)
Cu-en-water*	2.399 (0.73)	2.516 (1.01)	2.418 (0.80)
CuHDO-en	1.383 (0.23)	1.674 (0.28)	2.677 (0.74)
CuHDO-en-water*	1.137 (0.12)	1.514 (0.19)	1.537 (0.20)

* water leached sample
** standard deviation
*** compound middle lamella

9.4. Conclusions

From the light microscopy study of thin sections of southern pine and Douglas-fir, it was found that ray cells and resin canals play important roles in enhancing chemical penetration. For copper-amine treatment, copper was concentrated in the highly lignified cell corners and compound middle lamella, due to the copper-lignin fixation reaction. For copper-HDO amine treatment, copper deposits on the surface of the cell walls were principally observed, with a much lower copper response in the lignified cell corner or middle lamella. This implied the preferential formation of a copper precipitate in wood.

The observation of crystalline copper solids in tracheid lumens and pits in copper-HDO ethylenediamine treated samples by SEM-EDX suggested the formation of $Cu(HDO)_2$ precipitate in wood. No such deposits were found in copper-amine treated samples.

The copper retention in the cell walls and compound middle lamella for copper-amine treatment was much higher than that for copper-HDO amine treatment. This was due to the preferential formation of $Cu(HDO)_2$ precipitate, leaving much less copper amine to react with the wood. The EDX results after water leaching confirmed that Cu-MEA treatment was more leach resistant to distilled water than the Cu-en treatment.

Chapter 10

Summary

This project described a comprehensive study of fixation chemistry of amine-copper wood preservatives, and consists of three major parts: a) the leaching study of copper amine and copper-HDO amine treated wood, b) the fixation of copper and nitrogen in wood, and in individual wood component, such as lignin, holocellulose, and extractives, and c) the distribution of copper element and $Cu(HDO)_2$ precipitate in the copper-amine and copper-HDO amine treated wood.

The initial leaching experiment focused on assessment of the influence of different amines on the fixation of copper in wood, and investigated the leachability of copper-amine and copper-HDO amine treated wood. In addition to distilled water, the leaching samples were exposed to a more aggressive citrate buffer leaching solution, attempting to obtain additional information on the relative stability of amine-copper complexes and simple copper precipitates formed in wood. For copper-amine treated wood, citrate buffer leaching removed significantly more copper and amine than distilled water. However, the copper-HDO amine treated wood displayed similar leaching resistance to both distilled water and citrate buffer. Of the five copper-amine treatments, wood treated with Cu-MEA and Cu-Polyim showed the greatest leaching resistance, while copper-diamine treatments, including Cu-en, Cu-DAP, and Cu-AEEA, had lower leaching resistance. $Cu(HDO)_2$ precipitate, which is a very stable copper compound in both distilled water and citrate buffer solution, formed during copper-HDO amine

treatment. It was found that amine reacted with wood irreversibly and that this was independent of the amine copper reaction. The residual amine to copper mole ratio retained is about 1.2 after water leaching and 1.1 after buffer leaching, suggesting the formation of copper amine complexes in wood. However, it was not possible, based on the leaching study alone, to identify whether copper-amine complexes formed with wood present as the mole ratio of copper to amine of 1:1 or 1:2.

Since AEEAH can behave as either monoethanolamine or diamine when chelated with copper, the influence of different mole ratios of copper to AEEAH on its leachability was investigated. The UV-Vis measurement found that, increasing the mole ratio of AEEAH to Cu moved the absorption maximum to higher wavelength, approaching the position of the maximum wavelength of the copper monoethanolamine system. Lowering the mole ratio of AEEAH to Cu, led to a shift of the maximum to lower wavelength, more similar to that for a copper-diamine system. This confirmed that, with the high mole ratio of AEEAH to Cu, the amine behaved as an ethanolamine, while at low mole ratio, AEEAH functioned as a diamine system. Further, the leaching experiment of CuHDO-AEEA treated wood showed that decreasing the mole ratio of AEEAH to Cu enhanced the leaching resistance.

The fixation mechanism of copper and nitrogen in copper amine and copper-HDO amine treated wood was studied through the reactions of selected amine, copper-amine, and copper-HDO amine solutions with solid wood as well as wood components. In order to gain further evidence as to which copper species were present in wood after fixation, FTIR, ESR and XPS spectroscopic investigations of the treated wood were conducted.

The FTIR spectra of amine treated wood showed the irreversible removal of the carboxylic acid group, suggesting the formation of an amine-acid salt. This was supported by the corresponding XPS spectra, in which two nitrogen peaks were observed, one consistent with an amine-acid salt, and the other compared well with an amine which was reacted with a phenolic hydroxyl group in wood lignin. The FTIR and XPS results addressed the important interaction between amine and wood. The copper-amine treatments also caused the loss of the carboxylic acid functionality, but in this case, the XPS results supported that the amine was bound to copper as well as reacting with wood. FTIR spectra of copper-HDO amine treated wood were very similar to those of copper-amine treatment. Although FTIR analysis was not able to identify the formation of $Cu(HDO)_2$ precipitate, XPS measurements confirmed its formation in copper-HDO amine treated wood. However, XPS was not capable for determining whether diaminecopper(II) compounds or aminecopper(II) compounds were formed in wood. The ESR spectra can provide further information about how nitrogen is coordinated to copper in the treated wood during fixation. It was found by ESR that in copper amine treated wood, the dominant copper complexes were those with two moles of amine and one mole of copper. For copper-HDO amine treatment, however, copper was present as the precipitate of $Cu(HDO)_2$.

In order to investigate the important reactions between the wood components and copper and amines, organosolv lignin, pectin, and Scots pine holocellulose were selected to represent the major reactive functionality in wood lignin and in hemicellulose. FTIR, XPS and ESR were used to identify the products formed. It was suggested that the

phenolic hydroxyl groups, ester groups in lignin and the carboxylic acid groups in hemicellulose were the major bonding sites for copper and amine. Both lignin and hemicellulse played a significant role in the fixation of copper or amine in copper-amine and copper-HDO amine treatments.

The fixation mechanism of copper and nitrogen in wood lignin was also studied through the reaction of vanillin, a lignin model compound, with a copper ethylenediamine solution. The reddish copper complex formed was extensively studied using FTIR, ESR, and X-ray single crystallography, and identified to be a complex of $Cu(vanillian)_2(H_2O)_2$. An X-ray structural analysis of a single crystal of the complex enabled the structure to be drawn. In this complex, the central copper was bonded to two oxygen atoms from the methoxyl groups in vanillin, and two oxygen atoms from water, in a planar arrangement. The very distorted octahedral configuration was completed by two Cu-O (phenolic) bonds. The elemental analysis confirmed that no ethylenediamine was retained during complex formation. This was the first determination of a crystal structure of copper-lignin model complex without containing any nitrogen. This study suggested that a similar reaction between ethylenediamine copper solution and lignin in wood would take place to form a stable lignin-copper complex, without nitrogen present.

Considering the important reactions between wood extractives and copper, the current study was expanded to investigate the reactions between the copper-amine solutions and extractives present in Douglas-fir and Scots pine. The interactions between the selected copper-amine and copper-HDO amine solutions with taxifolin from Dougals-fir were also studied. The reaction products were identified by FTIR, XPS and ESR. It

was found that extractives from Scots pine heartwood and Douglas-fir heartwood reacted vigorously with Cu-MEA and Cu-Polyim to produce green precipitates. The diamine-copper system including Cu-en, Cu-DAP, and Cu-AEEA showed much lower reactivity with the same extractives. During the reaction of taxifolin and Cu-MEA, a green precipitate was produced, while brown precipitates were formed in the reactions of taxifolin and Cu-en and CuHDO-en. XPS analysis revealed that amine remained in the copper-taxifolin complexes, and ESR provided the additional information that the central copper in the copper complex formed is coordinated to two amines. For the reaction of taxifolin and CuHDO-en, no evidence supported the formation of $Cu(HDO)_2$ precipitate. The ketone group and hydroxyl groups on the C and B rings, respectively, were considered the major positions responsible for the copper chelation. Since chrysin has a very similar molecule structure to taxifolin, an attempt was made to investigate the reaction between chrysin and ammoniacal copper sulphate to compare it to the corresponding reaction between taxifolin and ammoniacal copper sulphate. A green precipitate was formed during the reaction, and the copper-chrysin complex formed did not contain any nitrogen. Since chrysin does not have the two hydroxyl groups in the B ring, and the hydroxyl group in the C ring, compared to taxifolin, it was postulated that in taxifolin, the most likely position for copper bound with ammonia is on the hydroxyl groups of the B ring.

The last part of this project was to seek the evidence to support the hypothesis that during treatment of wood with copper-HDO amine, $Cu(HDO)_2$ precipitate was preferentially formed. Useful information was obtained on the distribution and location of

copper in copper-amine and copper-HDO amine treated wood using light microscopy and SEM-EDX. From the light microscopic study of thin sections of impregnated southern pine and Douglas-fir, it was found that copper was concentrated in the highly lignified cell corners and compound middle lamella, due to the copper-lignin fixation reaction. For copper-HDO amine treatment, copper deposits on the surface of the cell walls were principally observed with a much lower copper response in the lignified areas. This implied preferential formation of a copper precipitate in wood. The observation of crystalline copper solids in ray cells and pits in CuHDO-en treated samples by SEM-EDX suggested the formation of $Cu(HDO)_2$ precipitate in wood. No such deposits were found in copper-amine treated samples.

Chapter 11

Recommendation for future research

The treatment of copper-amine or copper-HDO amine preservatives provides abundant nitrogen in wood. It is possible, therefore, that the higher nitrogen content in the wood after treatment, could be utilized by wood destroying fungi. In order to understand the biological activity of copper when complexed with amine or precipitated with HDO, the biological performance of copper-HDO and copper amine should be studied.

The current leaching study found that the copper depletion during citrate buffer leaching was not only caused by copper precipitates, but also by copper-wood complexes without amine, and copper-amine-wood complexes formed during fixation. A more intensive investigation of the relative leachability of copper complexes formed with lignin against those formed with hemicellulose is recommended to clarify what type of copper-amine-wood complex is responsible for the loss of copper in the buffer solution.

The fixation study of copper with wood components and the study of copper distribution in the treated wood highlight the interaction of copper and lignin as one of the dominant reactions occurring in wood during fixation. Future work should quantify the various contributions that wood components (wood lignin, hemicellulose, cellulose, and extractives) could make individually and collectively to the fixation of copper. Additional quantitative analyses of the reactions between copper and lignin, as well as copper and hemicelllose are necessary to find out the relative importance of the reactions of copper with the wood components.

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