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Title: Vapor Copper - A Potential Wood Preservative

Abstract
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This study seeks to determine the feasibility of
utilizing one vaporizable copper compound - bis-[1-
(dimethylamino)-2-propanolato] copper(II) (Cu(DMAP)$_2$ as a
potential wood preservative. The synthesis of Cu(DMAP)$_2$
was conducted in accordance with a method developed by
Buhro and Dingman, Washington University, St. Louis,
Missouri. The yields of Cu(DMAP)$_2$ synthesis were about
58%.

Preservative treatment of oriented strand board(OSB)
using Cu(DMAP)$_2$ applied in the vapor phase was
investigated. Under optimum conditions complete
penetration of OSB was achieved. In addition, commercial
levels of copper retentions was obtained. Treatment time
and temperature has a major influence on copper retention
and penetration. The leachability test of Cu(DMAP)$_2$ was
performed using a modification of AWPA Standard E-11 and

results told us that Cu(DMAP)$_2$ and ammoniacal copper sulfate (ACS) had similar leaching behavior.

The efficacy of Cu(DMAP)$_2$ as a preservative was assessed using soil block test and compared to ACS and chromated copper arsenate (CCA). Cu(DMAP)$_2$ was slightly more effective than ACS at low retention in leached samples, but it was slightly less effective than either ACS or CCA at higher retentions.

Vapor Copper - A Potential Wood Preservative

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Wenlong He, Author

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CHAPTER I

INTRODUCTION

Wood-based composites represent one of the fastest growing segments of the forest products industry (National Research Council, 1990). Initially, composite wood materials were developed either to utilize wood waste from other operations, to produce products such as medium density fiberboard, or to produce wood components with properties superior to those of solid wood , for example, plywood and glulam. Most of the early products were designed for interior non-structural uses, but composites are increasingly being utilized in exterior applications and frequently are the principle structural elements in a building (Barnes and Amburgey, 1993). With flakeboard, for instance, early products consisted of relatively small wood chips pressed together in random orientation. Today, however, flake geometry and orientation are closely monitored during production to yield products with specific properties. Fiberboards no longer are used only as a "skin" in interior applications; rather, fiberboard products are used in exterior exposure for both roofing and

siding. Molded wall panels are now being produced with the composite acting as both a skin and a structural element. With these changing uses has come increased exposure of composites to wetting, and consequently, to attack by decay fungi and insects. This, in turn, has stimulated research to develop new procedures and preservatives for protecting composite products from biodeterioration.

OBJECTIVE

The objective of this research was to determine the feasibility of utilizing a vaporizable copper compound as a wood preservative.

LITERATURE REVIEW

Composites such as plywood and laminated beams have long been treated with a variety of preservatives with relatively little difficulty; however, waferboard, oriented strand board (OSB), particleboard, and other composites are less amenable to preservative treatment. Most of these materials are relatively easy to impregnate with preservative solutions owing to the multitude of flow paths present. But the ingress of fluid often creates a permanent and unacceptable swelling which degrades the appearance and

decreases many board properties such as internal bond strength (Barnes and Amburgey, 1993). Perhaps more importantly, the need for post treatment drying increases costs and the potential for initiating degradation of the product.

A number of studies have been performed on preservative treatment of composites. Several researchers have investigated impregnation of plywood products (Viitanen, 1984; Orsler, 1987). A significant amount of research has also been undertaken on the effect of such treatments on the mechanical and physical properties of boards and reductions in such properties have been noted, especially at higher chemical loadings (Winandy et al, 1988).

Many technologies have been developed for the protection of wood composites. These technologies include increasing durability without biocides, incorporating additives into the resin, supercritical fluid treatment, wood modification, and vapor-phase treatment.

Increase Durability without Biocides

It is possible to increase the resistance of composite products to biodeterioration without the use of biocides, but such measures should be relied upon only in regions of low to moderate hazard from biodeterioration.

For instance, composites fabricated from furnish containing wood from both naturally susceptible (e.g., pine or mixed hardwoods) and naturally durable species (e.g., *Sequoia sempervirens, Thuja plicata, T. occidentalis*) are more resistant to both fungi and insects than are those made from furnish consisting of wood from only non-decay resistant species (Clark 1960, Behr 1972 Becker 1971), Alternatively, increasing the water repellency of composites decreases the probability that they will be colonized by decay fungi and insects. Composites fabricated from furnish that has been chemically modified (e.g., plasticized) may be highly resistant to biodeterioration. This method has certain limitations and is not widely used today because of the cost of the modifiers.

Increase Durability with Biocides

Most methods used to protect wood involve application of chemicals. Theoretically, it should be easier to achieve a uniform distribution of wood preservatives in composites than in solid wood products. Uniform treatment might be achieved by adding biocides to the wood furnish, to the resins or other additives during blending. With glulam beams, the individual laminates could be treated prior to gluing or the finished beam

could be treated. Composite treatment strategies include conventional treatment, incorporating a preservative additive, supercritical fluid treatment, wood modification through chemicals, and vapor-phase treatment.

Conventional Treatment

Pressure impregnation processes are, without doubt, the most important and successful industrial methods for applying wood preservatives. Composites are usually impregnated with solutions of fire retardant chemicals or biocides. The solutions are usually aqueous, producing undesirable swelling and strength reduction of the panel. The recent problems experienced with the performance of some fire retardant treated plywood in the USA illustrates the risks involved in this form of treatment if procedures are not rigorously followed. Incorporation of preservatives or fire retardants into the furnish prior to processing also presents problems in that a number of preservatives (e.g., phosphates, boric acid) have been found to interfere with bonding of the composites (Murphy, et al., 1993). Other problems exist with the disposal of preservative treated wastes arising from trimmings or from any surfacing treatments such as sanding.

Incorporating an Additive

It is possible to incorporate a preservative additive into the composite during its manufacture. This can decrease the cost of the final product in comparison with conventional pressure treatment of a finished panel and give a superior product in which the composite has a constant loading of preservative throughout its thickness rather than the "shell" treatment commonly present in treated solid wood products. The preservative-containing composite can be machined without loss of biological resistance. An added benefit is that the need to handle biocides is limited to a single manufacturing site.

In India, a group of research scientists investigated the preservative treatment of bamboo mat boards (Padmanabhan et al. 1993). Based on their preliminary trials, they identified following methods for further panel protection: treatment of mats before boards are manufactured; incorporation of preservative chemicals in the adhesive during board manufacture; and treatment after the boards were made. Incorporating preservative into adhesives was the most cost effective method.

The use of preservative additives may also offer a method for recycling treated solid wood by comminuting it to strands or other particle form, then consolidating with an adhesive into structural composite lumber or panels.

Such products could be used as home decks and timber bridges, or as utility poles or railway ties (Laks and Palardy, 1993). The use of preservative additives in wood composites is not necessarily a simple operation. A number of factors must be considered when developing such systems.

Modern wood composite manufacturing processes are often finely balanced systems. The factors which affect preserved composite performance include the interaction between the additive and adhesive, the nature of the additive, the nature of the furnish, and the method of incorporation. The addition of another chemical such as a powdered preservative may have major effects on the properties of the product if other aspects of the process are not modified. In addition, the effects of the processing parameters on the additive may be important. The characteristic of a preservative additive and the nature of the composite may also affect the properties of the final product in many ways.

Interactions with the adhesive

Perhaps the most obvious way in which an additive can have a detrimental effect on the properties of the composite is through interference with bond formation. An excellent example of this is the interaction of water-

soluble borates with phenol-formaldehyde (PF) resins. Bond strengths of PF-bonded waferboard containing biologically-effective levels of sodium borates or boric acid are unacceptably low (Laks et al, 1988). This is most likely due to gelling of the phenolic adhesive by the borate before the glue droplet can wet, transfer to, and penetrate the opposite wood surface (Vick et al., 1990). The gelling effect can be reduced by minimizing the availability of the borate to the adhesive droplet or particle by using borates with low water solubility or a low rate of solubilization.

In general, available evidence suggests that polymeric diphenylmethane diisocyanate (PMDI) adhesive is less prone to interference problems than phenol-formaldehyde (PF) resins. For example, the bonding of PMDI resins is not affected by soluble borates (Laks et al., 1988). However, Schmidt and Gertjejansen (1988) reported interactions between a triazole fungicide, azaconazole (1-[[2',4'-di-chlorophenyl)-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole), and PMDI. They used two methods of incorporation-blending the powdered fungicide with the flakes, and dissolving the additive in the resin prior to blending. The antifungal properties of composites made with first method were better than that made by the second route. Interactions between a potential additive and the

adhesive must be carefully defined for any manufacturing
processes.

Additives incorporated as insoluble powders may also
affect the adhesive through the physical presence of the
powder. Laks et al. (1991) performed an extensive
comparison between sodium borate (TIM-BOR[R]) and zinc borate
(FirebRake ZB[R]) as additives for PMDI-bonded waferboard
composite. They found that the two additives had differing
effects on bonding as their loading increased. The
internal bond strength (IB) of the sodium borate boards
remain reasonably constant as additive content rose, while
IB dropped as zinc borate content increased. These results
probably reflect water solubility of the additive. Sodium
borates are probably dissolved in the water contained in
the flakes. Zinc borate is much less soluble in water, and
would stay mainly as a powder on the flake surface, thereby
increasing the surface area of solids within the mat and
reducing the bonding efficiency of the adhesive. These
differences may account for the lower IBs observed as zinc
borate content increased.

Nature of the Additive

A number of factors affect the preservative efficacy
of fungicide or insecticide additives in a wood composite

systems (Laks et al., 1990). Ideally, the additive should not:

* interfere with adhesive bond formation

* degrade under pressing conditions

* be highly volatile during pressing

* affect the strength properties of the wood furnish

* leach out of the composite through weathering

However, some degree of mobility for the additive is desirable, either through volatility, or limited solubilization and diffusion during the pressing process. Anti-fungal additives cannot be completely immobile, because the biocide needs to diffuse into the cell walls of the flakes to be effective. If the additive stays as a discrete particle in the consolidated composite, the fungal mycelium could simply grow through the wood material and avoid the fungicide altogether. For example, chlorthalonil (CTL) is an excellent fungicide for wood preservative use, having similar or better antifungal activity than pentachlorophenol when compared in organic solvent systems(Laks et al., 1992). But aspen waferboard panels made incorporating CTL as a powder had little or no protective effect against two common decay fungi, even when incorporated at a relatively high loading of 8.4 kg/m^3. The poor performance of the CTL in this application may be due to its very low water solubility (0.6ppm at 25°C) and lack

of any significant steam volatility. It seems likely that the CTL remains as small particles between the wood wafers and is not able to protect the wood matrix because it is not present in the cell walls.

Preservative microdistribution can have important effects on anti-fungal properties, and fungal hyphae can grow through untreated cell walls to avoid particles of fungicide.

It is also possible for an additive to have a direct effect on the strength properties of the wood furnish. High levels of sodium borate in waferboard cause large reductions in MOR regardless of the adhesive used (Laks et al., 1988). This may be due to embrittlement of the wood furnish caused by the borate ion.

Nature of the furnish

The wood species used and the dimensions of the wood elements making up the furnish may also affect the properties of the preserved composite. Generally, hardwoods such as aspen which have a low density, as well as low lignin and extractive content are more prone to decay fungi than softwoods (Zabel and Morrell, 1992). If possible, it is clearly more desirable to use an inherently more decay resistant wood species as furnish for manufacture of a preserved composite.

The ability of an additive to diffuse into the wood element making up the composite determines its suitability to be used in that particular composite type. The thicker the wood particle, the more important diffusivity becomes. With the sodium borates, the size of the wood element is relatively unimportant because these additives can diffuse readily through moist wood (Morrell et al 1990). As long as there is compatibility with adhesive, this could allow the use of sodium borates in composites such as Parallam[R] where the transverse dimensions of the strands are relatively large. However, the water solubility of these borates and their subsequent ease of leaching would restrict the use of such a composite to protected applications with a minimal leaching hazard.

Method of Incorporation

Additives can be incorporated into a wood composite through a number of routes (Laks and Palardy, 1993). In the case of waferboard or oriented strand board, these include:

(A): Treatment of flakes, before or after drying, using an additional sprayhead or blender system.

(B): Mixing the chemical with the adhesive or wax which is subsequently applied to the flake in the blender.

(C): Spraying the flakes with a preservative solution or emulsion, or mixing the powdered chemical with the flakes in the blender.

(D): Metering a powdered preservative into the dried flakes immediately before the blender. The powder is then mixed with the flakes in the blender.

The application method has a greater effect on the decay resistance properties of a composite incorporating a fungicide. The best method will be depend on the properties of the additive and the adhesive. A better understanding of how the incorporation of a biocide additive affects the physical properties of a wood composite, and also how the manufacturing process affects the biological properties of the preservative will be required before these technologies experience extensive use in North America.

Supercritical Fluid Treatment

A new approach to modifying treatment fluid characteristics which has the potential for penetration of refractory woods is to utilize supercritical fluids as carrier solvents (Ito et al. 1984). In the supercritical region, there is no phase boundary between liquid and gas. A cooperative project sponsored by EPRI and co-sponsored by CSI, Inc. (Charlotte, NC), involves research between Oregon

State University and Mississippi State University. This project evaluated supercritical fluid treatment for wood products. Preliminary results are encouraging, but considerably more research is needed before the technical viability of this method is determined.

Wood Modification

Researchers have long sought methods for improving wood properties through modification. Any treatise on wood protection should include information on this approach to wood protection. This method uses modifying agents that react with the wood constituents to form cross-linkages. These cross-linkages reduce the hygroscopicity of wood making it less susceptible to attack from biotic agents. The challenge is to produce modified wood with a low weight gain and without losses in properties common to current methods such as acetylation. New generation polymer systems may have some application to composite materials.

Successful uses of biocides on composites must consider the effect of the biocide on the physical properties of the composite, the chemical interaction with the resin system used, the distribution of the biocide within the composite, the efficacy of the final treated composite, and the effect of manufacturing on properties and on the workplace environment. Further research will be

required for many newer technologies available to composite material protection to ensure that these effects are more thoroughly understood.

Vapor-Phase Treatment

One of the most exciting technologies for composite protection is based on the suggestion by Scheurch in 1968 that treatment in the vapor phase could mitigate problems that occur when treating with liquids. All treatments in the liquid phase depend upon the movement of liquid preservative into the wood. Two problems must be overcome in order to obtain deep, uniform treatment. First, tension forces at the liquid-air and liquid-wood interfaces must be overcome (Skaar 1972). Second, transverse movement is dictated by the permeability of pit membranes (Hunt and Garratt 1967). Pits may be aspirated, encrusted with extractives, or blocked by air embolisms that make them impervious to liquid flow (Kelso 1962, MacLean 1952, Miller and Graham 1963, Ruddick 1980, Thompson and Koch 1981). Vapor phase treatment was proposed by Shuerch (1968) for wood drying and wood modification. Barnes et al. (1969) evaluated several vapor phase chemical treatments for dimensional stabilization of wood. Ethylene oxide was effective, but treatment with vinyl chlorides was not successful (Barnes et al, 1969). Gas-phase treatments have

been used extensively for remedial treatment of wood in service (Morrell and Corden 1986, Morrell et al. 1986). Efforts to modify wood using gaseous reagents have met with only moderate success(Barnes et al. 1969, McMillin 1963). Reaction with alkylene oxides has yielded some decay and termite resistance (Rowell and Gutzmer 1975, Rowell et al. 1979), but these treatments have received little commercial interest because of the high loading of reactants required to achieve protection.

Vapor-Boron Treatment

One successful vapor-phase treatment is vapor boron which resulted from cooperative research between Imperial College, London, U.K. and the Forest Research Institute, Rotorua, New Zealand. Vapor phase boron treatments have been applied as primary treatments for wood and wood-based materials (Turner and Murphy 1987, Turner et al. 1990). This process is based upon the volatilization of trimethyl borate, which penetrates the wood as a gas where it reacts with moisture in the wood to deposit boric acid (Murphy et al., 1993). Boron compounds are broadly effective, low toxicity biocides which have been used for many years in a variety of environments. The vapor boron process is limited to materials with moisture levels below 6 to 8%. At moisture levels above this range, excessive water leads

to rapid reaction near the wood surface, resulting in poor boron distribution. The biggest problem of this system is that vapor boron could rapidly leach from materials subjected to continuous moisture, making these treatments unacceptable for use in many areas where preservative protection is essential.

Despite the limitations of vapor boron, the concept of using a strong vacuum to volatilize a water-reactive biocide which then permeates the wood-based material and reacts with any moisture present has numerous advantages over conventional treatment processes. The absence of residual solvent, the lack of swelling or deformation, and the elimination of any need for post-treatment drying would all provide a strong incentive for development of leach-resistant vapor type processes.

Copper compounds are well known biocides. Copper(II) has been used as a wood preservative since 1600 B.C. (Zhou, 1991). In 1926, Gilbert Gunn of the 'Celcure' company of Scotland, successfully achieved the fixation of copper in treated wood. In 1933, an Indian Government research worker, Sonti Kamesam, used chromium to fix both arsenic and copper in treated wood. The preservative was known as "Ascu" (Wilkinson, 1979). Since the early 1930's, chromated copper arsenate (CCA) has become the most widely used waterborne preservative. Other popular copper-based

preservatives are ammoniacal copper arsenate (ACA), ammoniacal copper zinc arsenate (ACZA), ammoniacal copper quat (ACQ), and ammoniacal copper citrate (ACC)(Xie et al, 1995). All of these compounds, however, are water soluble and induce the same swelling problems typical of waterborne preservative. One alternative is to use the most volatile copper(II) compounds, such bis-(1-dimethylamino-2-propanolato) copper(II), as potential wood preservatives. These materials behave in a manner similar to vapor borne compounds, but the copper may be less susceptible to leaching.

CHAPTER II

SYNTHESIS OF VAPOR COPPER

INTRODUCTION

The discovery of high temperature superconductors in the 1980's spurred the search for volatile copper compounds. These compounds were needed for vapor deposition on those new superconductors. As a result, several volatile copper compounds were discovered (Purdy et al. 1991). The most volatile copper(II) compound known is bis[1-(dimethylamino)-2-propanolato] copper(II) (Cu(DMAP)$_2$). Its formula is Cu[OH(CH$_3$)CH$_2$N(CH$_3$)$_2$]$_2$.

This compound sublimes over a temperature range of roughly 60°C t0 140°C (Buhro, 1994). Above this temperature, the compound begins to decompose. The melting point is 134-135°C. It is soluble in common organic solvents such as benzene, toluene, and hexane. It is a dark-purple solid that is sensitive to water and oxygen. The preparation of this compound has been studied and its structure determined (Goel et al., 1990). Copper(II) alkoxide is typically prepared by alcohol-interchange reactions with dimethoxy copper(II). Dimethoxy copper(II) has been prepared by the decomposition of methyl copper(I)

in MeOH in the presence of and by the reaction of CuX_2 (X=Cl, Br) and MOMe (M=Li, Na) (Costa et al., 1965 and Brubaker et al., 1965).

The following procedures describe two synthesis methods. (I): dimethoxy copper(II) by alcohol interchange, and (II): an exchange reaction with sodium alkoxide and copper tosylate.

SYNTHESIS PRINCIPLES

Alcohol interchange

$$Li + MeOH \rightarrow LiOMe + 0.5\ H_2$$

$$2LiOMe + CuCl_2 \rightarrow Cu(OMe)_2 + 2\ LiCl$$

$$Cu(OMe)_2 + 2HOCHMeCH_2NMe_2 \rightarrow Cu(OCHMeCH_2NMe_2)_2 + 2MeOH$$

Exchange of sodium alkoxide and copper tosylate

$$CuO + 2HOTs \rightarrow Cu(OTs)_2 + H_2O$$

$$Na + HOCHMeCH_2NMe_2 \rightarrow NaOCHMeCH_2NMe_2 + 0.5\ H_2$$

$$2NaOCHMeCH_2NMe_2 + Cu(OTs)_2 \rightarrow Cu(OCHMeCH_2NMe_2)_2 + 2NaOTs$$
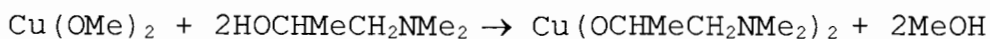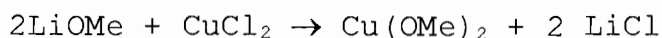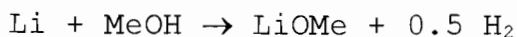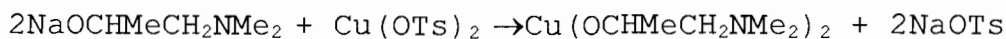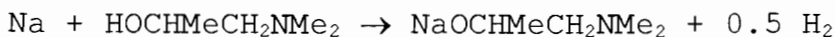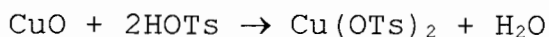
PROCEDURES

Alcohol interchange procedures

Preparation of Lithium Methoxide

All ambient-pressure operations were carried out under purified nitrogen using oxygen- and moisture-free solvent in a dry box (32″ x 24″ x 38″).

The impurity coating was removed from lithium wire by scraping the surface of the wire in the dry box. A 500ml round-bottom flask was charged with cleaned lithium wire (2.4g, 346mmol) and a magnetic stirring bar. Then anhydrous MeOH (300ml) was added to the cooled flask in about 5 minutes resulting in a controlled exothermic reaction. The stirring mixture was allowed to warm to room temperature over about 4 hours to complete the disappearance of the lithium wire and the generation of LiOMe (a clear, transparent solution).

Preparation of Dimethoxycopper(II)

Anhydrous copper(II) chloride (23.5g, 175mmol) and MeOH (200ml) were combined in an oven-dry 1000ml round bottom flask equipped with a magnetic stirring bar. Then the LiOMe solution which was made in the first step was transformed by stirring copper(II) in chloride solution.

An exothermic reaction ensued and a blue precipitate formed in about 10 minutes.

The reaction mixture was stirred for about 18 hours at room temperature, and the blue solid was then collected in a 350ml filter funnel. The LiCl byproduct and other side products were extracted from the blue dimethoxycopper(II) by vigorously shaking the collected precipitate with 200ml MeOH in the filter funnel, followed by removal of the MeOH extract. This process was repeated until a silver-nitrate test for chloride ion in the extract was negative. During each extraction, the mixture was shaken vigorously enough to break up the solid cake. Ten such washings were usually adequate for removing the LiCl and side products. The dimethoxycopper(II) product was finally dried under reduced pressure. Average yield was 19.8g (90.2% yield).

Preparation of Cu(DMAP)$_2$

A suspension of Cu(OMe)$_2$ (9.72g, 77.4mmol) was prepared in 250ml of benzene in an oven-dry 500ml flask equipped with a magnetic stirring bar. 1-dimethylamino-2-propanol (19.2ml, 16.0g, 155.8mmol) was added with stirring and the flask was fitted with a 300mm fractionating column and a variable-return distillation head. A deep-purple homogeneous solution was formed within 30 minutes at room

temperature. The solution was heated gently (50-60°C) for 3 hours, and then was heated to reflux. The MeOH librated during the reaction was removed as a benzene/MeOH azeotrope (B.P.: 58.3-80.2°C) and was collected at a rate of 1-2 drops per minute over 12-18 hours. When the cessation of MeOH libration was achieved, the solution was cooled and the solvent removed under reduced pressure. The residual dark-purple solid was purified by sublimation (90°C bath/10^{-1}Torr) to give bis[1-(dimethylamino)-2-propanolato] copper(II) as dark-purple crystals. The crystals were analyzed with an Asoma model 8620 X-ray fluorescence (XRF) analyzer, which indicated a copper content of 21.44 percent, compared with a calculated content of 23.72 percent. Average yield was 13.1g (63.4% yield).

Exchange of sodium alkoxide and copper tosylate

Preparation of Copper(II)p-Toluensulfonate

This is a simple acid-base reaction in which two equivalents of HOTs (p-Toluenesulfonic acid) combined with CuO to form the copper toluensulfonate hexahydrate (Cu(OTs)$_2\bullet$6H$_2$O) complex. The reaction required no special handling procedures and was carried out under air. The reaction used a slight excess of CuO, which was easily removed by filtration during workup. This complex was

dried in a vacuum oven to remove all water from crystallization. The water was weakly bound to the copper which allowed for easy removal.

CuO (32.47 grams, 0.408mol) and 150.18 grams of HOTs (0.789mol) were weighed into a 1000ml round bottom flask. Deionized water (700ml) was added to the flask and a reflux condensor was attached. The mixture was stirred and refluxed for 4 hours. After refluxing, the deep blue solution was filtered to remove excess CuO. The solution was concentrated on a Rotovaporator, and the concentrated solution was allowed to crystallize. The crystals were collected by filtration and washed with about 300ml of hot toluene to remove residual HOTs. The light blue crystals were collected by filtration and dried in a vacuum oven at 100°C for 24 hours. The product was anhydrous and became a uniform bright greenish yellow. Average yield was 128.72g (73.1% yield).

Preparation of Sodium Dimethylamino-2-Propanolate

This procedure was performed under an atmosphere of purified nitrogen as the reaction and its components were sensitive to the moisture in the air.

Sodium metal was handled under a nitrogen atmosphere and the surface cleaned with a spatula to remove residual sodium oxide. Sodium (8.7 grams, 0.378mol) was placed in a

1000ml flask along with a magnetic stir bar and 600ml of dry, deoxygenated hexane. Dimethylamino-2-propanol (38.98 grams, 0.378mol) was then weighed into a 60ml syringe. The amino-alcohol was added drop-wise over a 5 minute period into the sodium/hexane flask while stirring. After complete addition of the amino-alcohol, the mixture was refluxed until no sodium remained (about 24 hours).

Preparation of the Bis[Dimethylamino-2-Propanolato] Copper (II) (Cu(DMAP)$_2$)

This is an exchange (metathesis) reaction of the sodium alkoxide and the copper tosylate to give the copper alkoxide. The reaction was run under nitrogen in a dry box.

Anhydrous copper(II) tosylate (74.0g, 0.182mol) that had been oven dried at 100°C for an hour prior to use to insure the reagent was completely anhydrous was placed in a 2000ml flask with a magnetic stir bar. Dry hexane (300ml) was added and the material was suspended in the hexane by stirring. The sodium alkoxide solution prepared in step 2 was then transfered into the mixture. The mixture was continually stirred for about 24 hours under a nitrogen atmosphere to insure complete mixing. A deep violet solution and a white suspension resulted. The solution was filtered to remove salts and the deep violet filtrate was

evaporated under vacuum to obtain $Cu(DMAP)_2$ solid. The copper alkoxide obtained was of reasonable purity, but further purification may be performed if necessary by sublimation. Actual yield was 35.24 g (80.29% yield).

RESULTS AND DISCUSSION

Yield of Alcohol Interchange Procedure

Yields of each reaction and overall reaction yield using the alcohol interchange procedure are shown in Table 2.1.1.

Table 2.1.1: Synthesis Yield of $Cu(DMAP)_2$ and $Cu(OMe)_2$ by the Alcohol Interchange Procedure

Product	Yield(%)	Reference Yield(%)[a]
$Cu(OMe)_2$	90.2	94
$Cu(DMAP)_2$	63.4	75
Overall	**57.2**	**70.5**

a): Data from Buhro, W. E., 1994.

The yield was lower than that of previous reports (Buhro, W.E., 1994). The dry box was not absolutely dry and the presence of small amounts of air or moisture might decrease yield. In addition, the reference yields were obtained using Schnlenk flasks that are specifically used

for air- and moisture-sensitive synthesis processes, while ours were performed using regular glass apparatus.

Yield of Exchange of the Sodium Alkoxide and the Copper Tosylate Procedure

The results of the exchange procedure are shown in Table 2.1.2.

Table 2.1.2: Synthesis Yield of $Cu(OTs)_2$ and $Cu(DMAP)_2$ by the Exchange Procedure

Product	Yield(%)
$Cu(OTs)_2$	73.1
$Cu(DMAP)_2$	80.29
Overall	**58.7**

The exchange procedure has some advantages over the alcohol interchange procedure. Sodium metal is cheaper and easier to handle than the lithium wire used in the alcohol interchange process and the first reaction can be performed in air. Most importantly cheaper substrates decrease the cost of production for $Cu(DMAP)_2$.

CHAPTER III

VAPOR COPPER TREATMENT PROCESS AND PERFORMANCE

INTRODUCTION

Preservation methods for composites must be both effective and environmentally acceptable. These general requirements (Murphy et al., 1993) for a preservative include:

1) Efficacy — an active ingredient effective in the composite against decay fungi and wood destroying insects.

2) Acceptable environmental characteristics for the treatment operation and treated products, including a final disposal strategy.

3) Mechanical properties — the treatment should not significantly reduce the mechanical properties of the composite.

4) Physical properties — minimal interference with physical properties such as dimensional stability and moisture relationships.

5) Appearance — the treatment should not alter the appearance of the product unless this is desired for identification purposes.

6) Speed and flexibility — treatment and any associated processing(e.g., drying) should be as rapid as possible and should be capable of providing treated product in sufficient volume to meet orders at short notice.

7) Verification and compliance with standards-treated materials should be readily analyzable for quality control purposes.

In the late 1980s a new approach to wood treatment based on the use of volatile borate esters was developed by researchers at Imperial College(IC), London and the Forest Research Institute, Rotorua, New Zealand (NZFRI). The process addresses many, if not all, of the requirements listed above for a modern wood treatment method and has since become known as the Vapor Boron Method or Treatment. However, vapor boron can rapidly leach from materials subjected to continuous moisture, making these treatments unacceptable for use in many areas where preservative protection is essential.

Despite the limitations of vapor boron, the concept of using a strong vacuum to volatilize a water reactive biocide which then permeates the wood-based material and reacts with any moisture present has numerous advantages over conventional treatment processes including:

- "Dry" process — no liquid carriers are necessary.

- Treatment is carried out on the manufactured composite and does not interfere with the pressing or bonding process.

- Treatment of the final manufactured product means no disposal problems with treated waste from trimming, sanding, and other finishing process.

- Only very slight effects on mechanical or physical properties of composites.

A preservative, by definition, must remain in wood for many years. Permanence depends on many factors, but two important ones are the physical and chemical properties of the preservative, and the way in which it is held in the wood. If treated wood is to be used in damp places, then the preservative must not wash out, or leach: to resist leaching it must either be naturally insoluble in water, or become chemically altered within the wood.

The term "fixation", as used in the field of wood preservation, refers to the mechanism by which preservative components become stabilized in the wood to resist leaching by rain or ground water. Many methods can be used to determine the leachability of preservative. In North America, the American Wood-Preservers Association Standard E-11 is often employed.

In addition, a wood preservative must ultimately prevent attack by wood-destroyers. A reliable measure of

effectiveness can be obtained from field and service tests, but this may take many years. A typical field trial, for example, could last for as long as 25 to 50 years. In order to save time, laboratory soil-block tests are often used to evaluate the efficacy.

MATERIALS AND METHODS

OSB Samples

Oriented strand boards (11mm thick) were obtained locally and conditioned by drying overnight at 105°C. The boards were cut into 19 x 19 x 11mm and 100 x 100 x 11mm samples. The 100mm samples were edge sealed with epoxy resin (ITW Revon[R]), where as the 19mm samples were not edge sealed. All samples were oven dried at 105°C before treatment.

Chemicals

Cu(DMAP)$_2$ was synthesized in accordance with a method developed by Buhro and Dingman at Washington University in St. Louis, Missouri (Buhro, 1995, private communication).

Ammoniacal copper solution was prepared by adding $CuSO4 \cdot 5H_2O$ to aqueous ammonia along with ammonium

bicarbonate at a rate of 1:1.1:0.75, respectively (Hulme, 1979).

CCA type C (oxide basis) was provided by CSI, Inc. (Charlotte, NC) as a 50-percent concentrate and was diluted with water and used without further modification.

Preservative Treatment

All $Cu(DMAP)_2$ treatments were performed in a dry-box under a nitrogen blanket (Figure 3.2.1). Four replicate samples per treatment were oven dried at 105°C and placed in a modified Aldrich sublimation apparatus (Figure 3.2.1.) equipped with a removable vacuum inlet with stopcock. A vacuum (0.9 torr) was applied, then $Cu(DMAP)_2$ gas was admitted to the treatment chamber which was placed into a hot bath preheated to 106, 112, or 120°C for 40, 80, or 120 minutes. The samples were then ground to pass a 40 mesh screen and the retention was determined by using an X-ray fluorescence spectrometer (XRF). Penetration was assessed by cutting the panels to reveal the inner surface and applying Chrome Azurol S to locate copper.

ACS and CCA samples were impregnated by immersing blocks in the desired treatment solution, raising the pressure to 800 kPa (116 psi), and holding it for 60 minutes. The pressure was then released and the samples

were weighed to determine solution uptake. These values
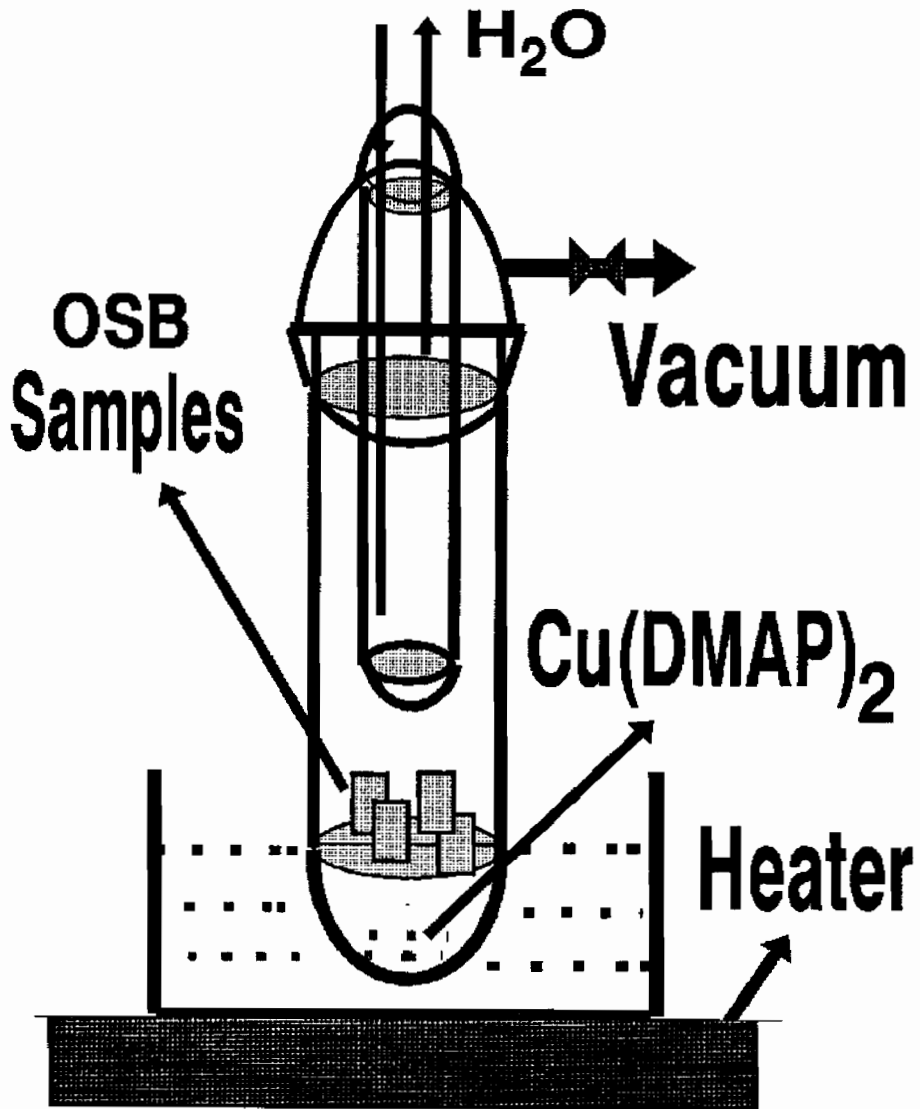
were used to calculate retentions.

Figure 3.2.1: Treatment Apparatus Used to Impregnate Samples with Vapor Copper

Assessment of Copper Distribution

The distribution of copper within the treated OSB was assessed visually after cross cutting one of four samples in half and spraying with copper indicator (Chrome Azurol S, AWPA Standard, A3-91). A deep blue color indicated the presence of copper. Penetration for each set of replicates was measured on both outer faces and described as the average depth from the outer face to the center of the sample.

Copper Leachability

OSB samples treated with $Cu(DMAP)_2$ and ACS to target retentions of 4, 2, 1 kg/m^3 (oxide basis) were used for leaching tests. Tests were performed using a modification of American Wood-Preservers Association Standard E-11 (AWPA, 1992). Block size was 19mm by 19mm by 11mm rather than the 19mm cube stated in the standard. The leachate was sampled and analyzed after 6, 24, and 48 hours, then at 48-hour intervals for the remainder of the 14-day period.

X-Ray Diffraction

A 1.08 g sample of pure $Cu(DMAP)_2$ was placed in 10.43 g of water and stirred for 15 minutes at room temperature. The purple solid turned blue-green and was

isolated via filtration, then allowed to dry at room temperature. The dried solid was analyzed with a Siemens D5000 diffractometer, equipped with a Kevex, Peltier cooled Si(Li) energy dispersive detector, and copper K_α radiation source. Measurements for Rietveld analysis were collected from 2 to 60° two-theta, with a step size of 0.002° and a count time of 0.6 sec/step. The width of the antiscatter and divergence slits were computer controlled to maintain the irradiated sample length at a constant value of 6 mm throughout the entire scan.

Decay Tests

Soil block tests were conducted in accordance with the ASTM Standard D1413-76 (ASTM, 1995) except samples were 19 x 19 x 11 mm in size rather than the 19mm cubes required. Samples were treated with vapor copper, ammoniacal copper sulfate, and CCA. The target retentions for vapor copper and ammoniacal copper sulfate were 1, 2, $4kg/m^3$, while blocks were only treated to $4kg/m^3$ with CCA (oxide basis). Both leached and unleached blocks were tested. Samples were oven-dried at 105°C and weighed prior to sterilization by exposure to 2.5 mrads ionizing radiation from a cobalt 60 source. French square bottles (225ml) with screw caps from which the liners had been removed were prepared. About $100cm^3$ of screened silt loam

(forest soil) were placed in each bottle and sufficient distilled water was added to raise the moisture content (MC) to 60% of the soil water holding capacity (WHC).

An untreated western hemlock (*Tsuga heterophylla* [Raf] Sarg) or red alder (*Alnus rubra* Bong) feeder strip measuring 35 x 15 x 3mm was placed centrally on the soil surface, and the bottle was tapped gently to level the surface of the soil. Red alder feeder strips were used for *Trametes versicolor* while western hemlock was used for *Gloeophyllum trabeum*. The filled bottles were then loosely capped, autoclaved for 45 minutes at 121°C, cooled overnight, and reautoclaved for 15 minutes at 121°C.

After cooling, each feeder strip was inoculated at diagonally opposite corners with a mycelial plug cut from the actively growing edge of a 7 day old malt agar culture of either *T. versicolor* or *G. trabeum*. The bottles were then incubated at 28°C and 75% R.H. until the feeder strips were heavily colonized (overgrown) by the test fungus.

One sterilized block was then placed on the feeder strip. Each treatment was replicated on 6 blocks. The wafers were incubated at 28°C for 12 weeks. At the conclusion of the incubation period, the test blocks were removed from the bottles with forceps, and gently scraped clean of adhering mycelium and soil. The blocks were then

oven-dried at 105°C prior to weighing to determine fungal induced weight loss.

RESULTS AND DISCUSSION

Vapor Copper Retention and Penetration

Preservative retention and penetration increased with both treatment time and temperature, Full penetration occurred after 80 minutes or longer at treatment temperatures of 112°C or higher (Table 3.2.1.). The improved penetration was associated with a proportional increase in retention. For example, penetration increased 32% and retention almost doubled when the temperature was increased from 106°C to 120°C in the 40 minute treatment. Increasing the temperature increased the vapor pressure of the $Cu(DMAP)_2$ and provided an increased differential pressure between the interior and exterior of the samples resulting in improved penetration. The higher vapor pressure also provided a higher concentration of $Cu(DMAP)_2$ in the vapor penetrating the sample, resulting in higher retentions. The results differed between large and small samples (Table 3.2.2.). Complete penetration of large samples was not achieved even when samples were treated at 120°C for 120 minutes. The highest retention of copper was 2.08 kg/m^3 (oxide basis). These poor results may be due to

limitations of the vacuum achieved.   Edge sealing may have

also limited penetration.

Table 3.2.1.: Retention(R) and copper penetration(P) in OSB
samples (19 x 19 x 11 mm) treated with Cu(DMAP)$_2$[a]

Temperature	106°C		112°C		120°C	
Time	R[b]	P[c]	R	P	R	P
(Min.)	kg/m^3	(%)	kg/m^3	(%)	kg/m^3	(%)
40	0.76	60.36	1.29	72.36	1.67	92.18
80	1.38	88.73	2.07	100.0	2.26	100.0
120	2.35	100.0	2.91	100.0	4.40	100.0

a) Values represent means of four replicates.
b) Retention, as determined by x-ray fluorescence spectroscopy
   of samples removed from each of four OSB blocks.
c) Penetration, values are based on the percentage of
   preservative penetration in each of the four blocks as
   measured with Chrome-Azurol S.

Table 3.2.2: Retention and copper penetration in OSB
samples(100 x 100 x 11mm) treated with Cu(DMAP)$_2$[a]

Temperature	120°C	
Time	Retention[b] as CuO	Penetration[c]
(min.)	(kg/m^3)	(%)
40	1.15	26.54
80	1.19	37.45
120	2.08	72.91

a) Values represent means of four replicates.
b) Retention, as determined by x-ray fluorescence spectrometer
   of samples removed from each of four OSB blocks.
c) Penetration, values are based on the percentage of
   preservative penetration in each of the four blocks as
   measured with Chrome-azurol S.

Leaching of Copper from Vapor Copper Treated Wood

Copper losses in blocks treated to the highest copper retentions ($4kg/m^3$ as CuO) were generally lower with Cu(DMAP)$_2$ than ACS (Figure 3.3.1A). Copper-amine complexes can complex with lignin model compounds (Xie et al. 1995). Thus, while Cu(DMAP)$_2$ should react with water in the panel to form the corresponding copper hydroxide, the isopropanol amine may still remain complexed with the copper. The resulting complex appeared to be more resistant than was ACS to leaching. Copper may also be fixed to the wood substrate through copper adsorption (Eadie and Wallace, 1962). The rate of leaching at lower retentions appeared to be slightly higher for Cu(DMAP)$_2$ than for ACS (Figure 3.3.1B and C). The effect of copper retention on subsequent susceptibility to leaching may indicate that the binding sites in the wood and the stability constants of the copper complex with those sites differ for the two compounds.
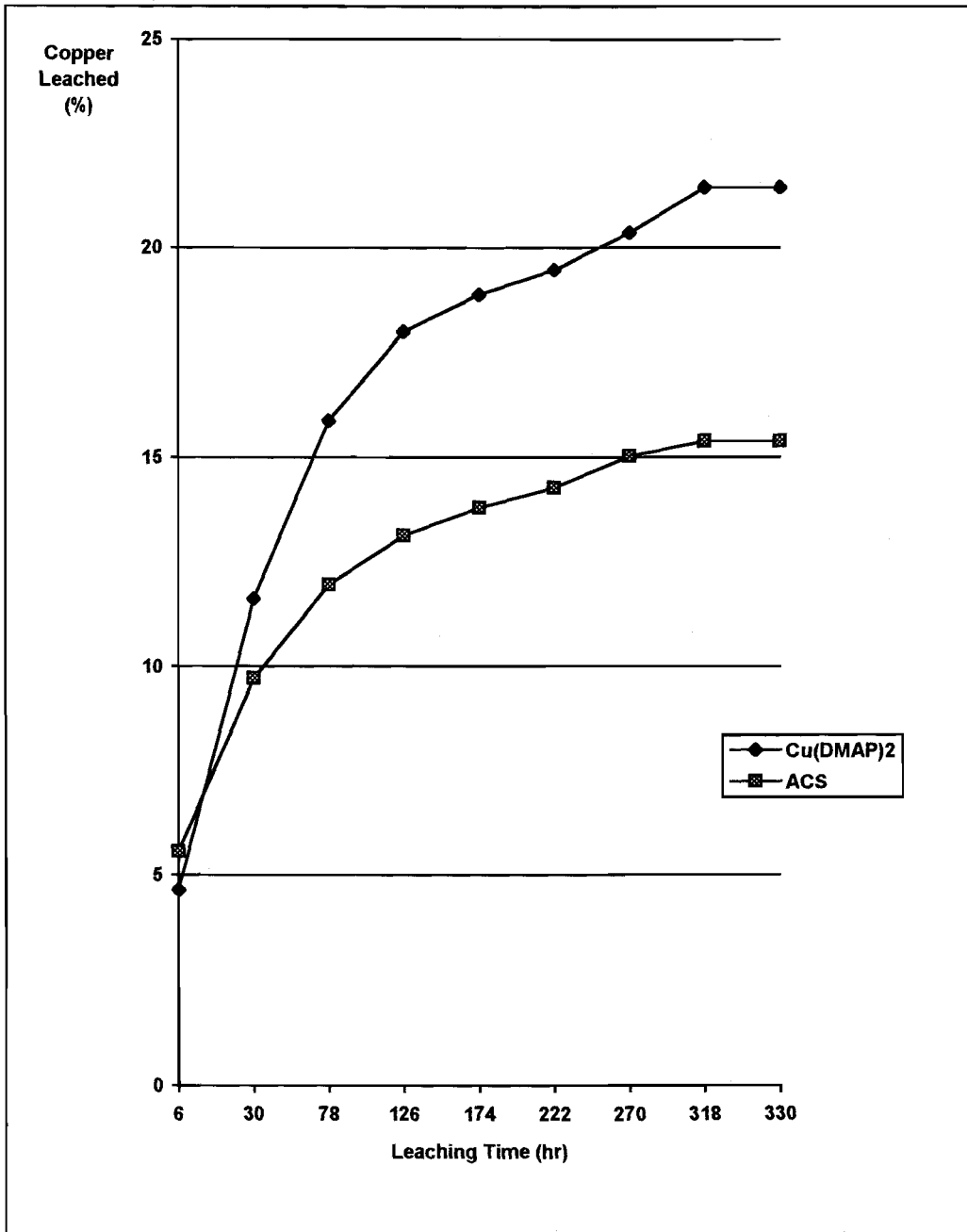
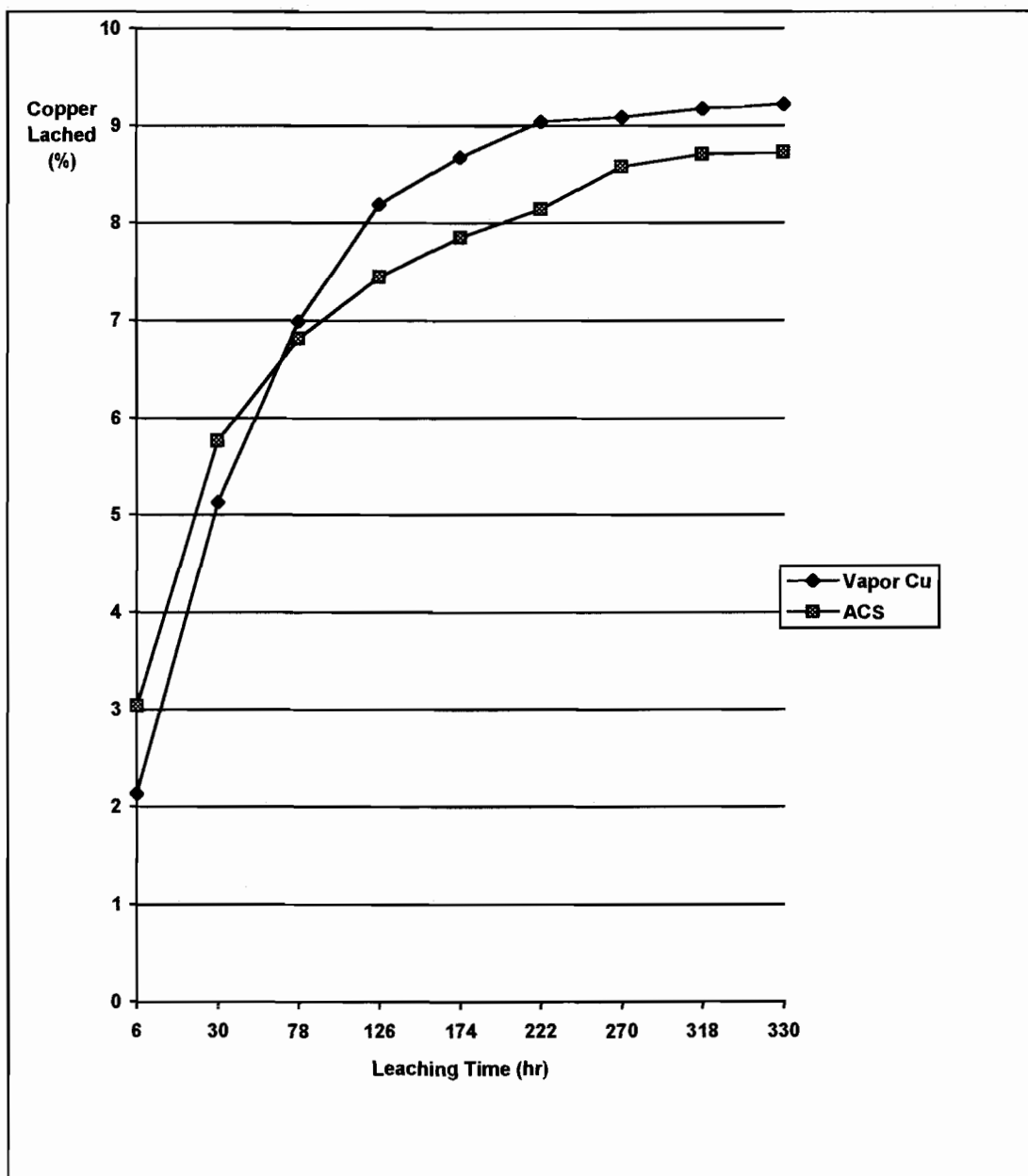**Figure 3.3.1A:** Leaching losses of copper from panel samples treated to 1.0kg/m³ with ACS or Cu(DMAP)₂

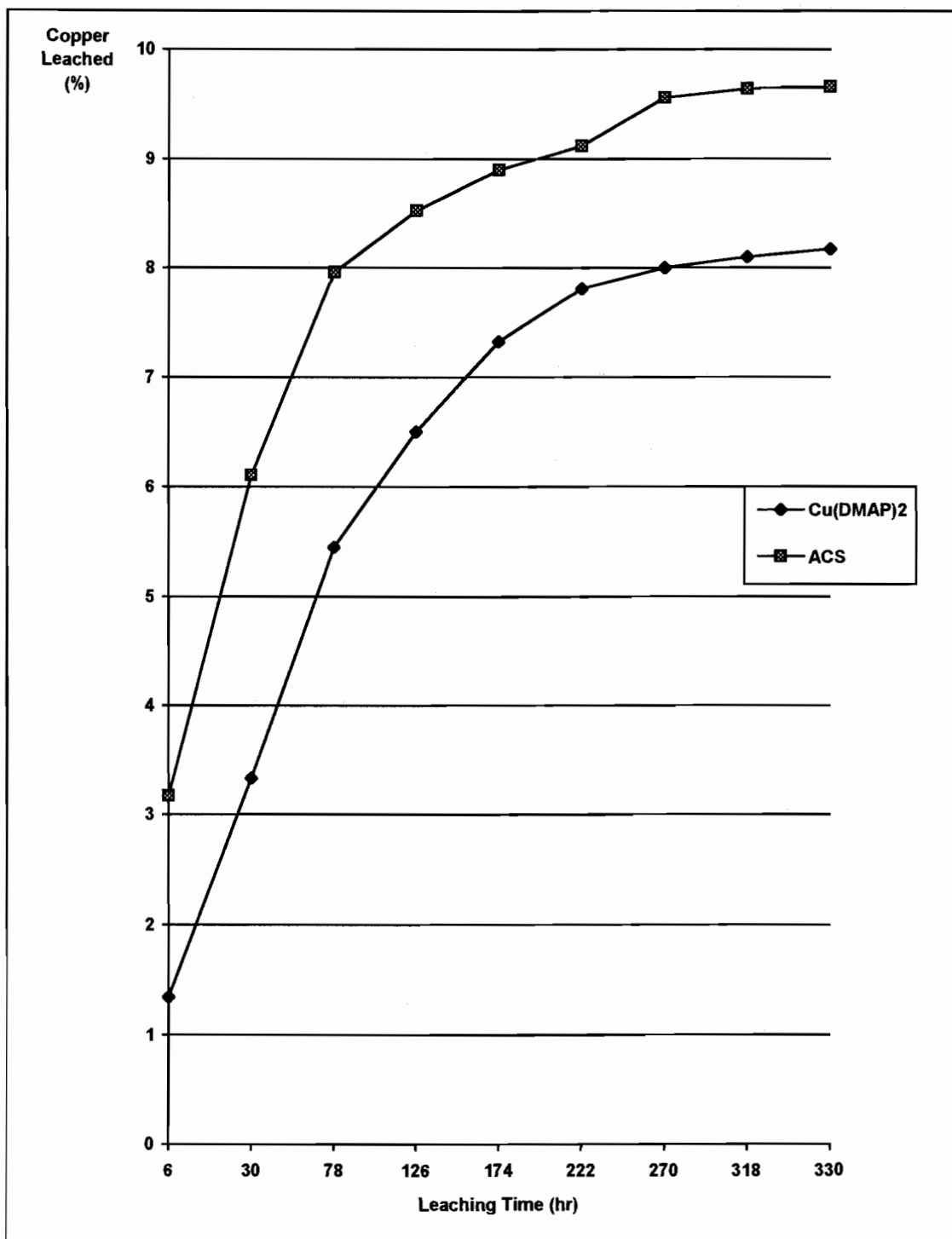**Figure 3.3.1B:** Leaching losses of copper from panel samples treated to 2.0kg/m^3 with ACS or Cu(DMAP)$_2$

Figure 3.3.1C: Leaching losses of copper from panel samples treated to 4.0kg/m^3 with ACS or $Cu(DMAP)_2$

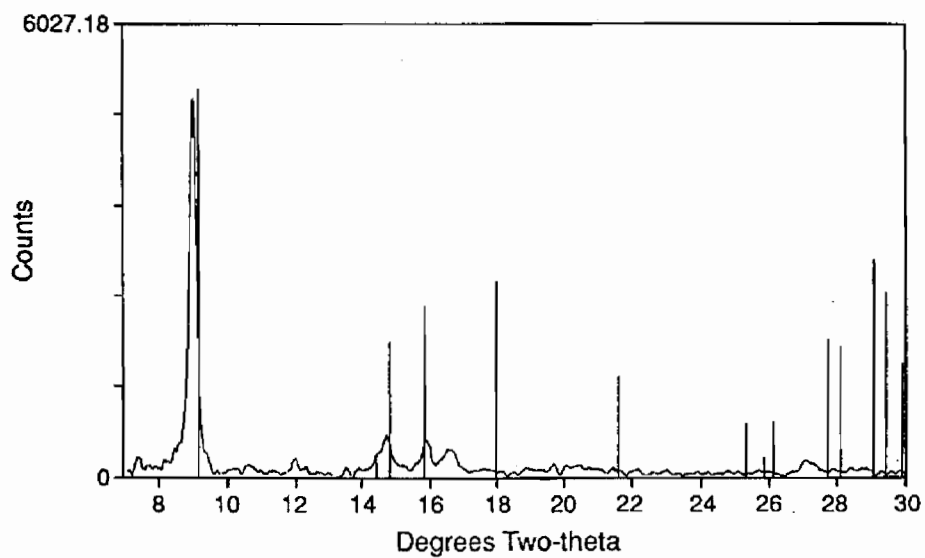Figure 3.4.1: X-ray diffraction analysis of hydrolyzed
Cu(DMAP)$_2$

X-Ray Diffraction Analysis

The spectrum of the hydrolyzed Cu(DMAP)$_2$ showed a reasonable match with Cu(OH)$_2$· xNH$_3$· yH$_2$O, indicating that the amine may remain complexed to the copper after hydrolysis (Figure 3.4.1.). The X-ray diffraction instrument did not have a standard file for Cu(DMAP)$_2$, so the data were largely circumstantial; however, the fits were poor for standard diffraction patterns for Cu(OH)$_2$ and CuCO$_3$. The literature suggests that many amines complex with copper in aqueous solution (Tauler and Casassas, 1989); these data support that hypothesis. The copper ethanolamine system has been shown to retain the amine ligands in the presence of lignin model compounds (Xie, et al., 1995). It seems likely that the DMAP ligand remains complexed with the copper ion in an aqueous environment. If true, this would suggest that leaching of DMAP from treated wood may be minimal.

Decay Resistance of composites treated with Vapor Copper

Weight losses of untreated samples exposed to *T. versicolor* were generally lower than those found with *G. trabeum* reflecting the use of a coniferous panel material and the use of a methodology which tended to favor brown rot fungi. Despite these differences, the magnitude of control weight losses permitted comparisons with the

various treatments for both fungi. Weight losses in leached blocks were generally larger than unleached samples, although the differences were sometimes slight (Table 3.4.1, 3.4.2.).

Weight losses for *T. versicolor* were low in samples treated to $4.0kg/m^3$ with all three chemicals regardless of leaching procedure (Table 3.4.1.). Weight losses steadily increased with decreasing copper level for both $Cu(DMAP)_2$ and ACS, although weight losses in $Cu(DMAP)_2$ treated blocks were lower than those for ACS at $1.0kg/m^3$. The results suggest that both chemicals have a threshold around $4.0kg/m^3$.

Weight losses associated with *G. trabeum* were generally greater than those found with *T. versicolor* and it was not possible to calculate a threshold for either $Cu(DMAP)_2$ or ACS at the concentrations tested (Table 3.4.2.). *Gloeophyllum trabeum* is not typically considered to be highly copper tolerant and its activity here against an array of copper systems is perplexing.

The results suggest that $Cu(DMAP)_2$ was unable to protect wood at the levels evaluated. While higher copper loadings might enhance activity, the levels tested are far in excess of those which normally confer protection to wood in tests of this nature.

Table 3.4.1.: Average weight losses in the OSB after treatment with selected preservative and exposure to *Trametes versicolor* in a modified soil-block test[a].

Chemical	Retention (kg/m^3)		Average weight loss(%)	
	Leached	Unleached	Leached	Unleached
Cu(DMAP)$_2$	4.99	4.76	6.51(2.9[b])	5.92(1.3)
Cu(DMAP)$_2$	2.98	2.13	21.5(4.1)	7.83(2.3)
Cu(DMAP)$_2$	1.17	1.13	25.5(5.1)	20.6(4.8)
ACS	4.32	4.32	1.01(0.3)	0.81(0.6)
ACS	1.95	1.95	4.91(0.5)	2.02(1.1)
ACS	1.02	1.02	34.3(3.7)	19.1(8.2)
CCA	4.03	4.03	2.80(0.9)	1.03(0.8)
Control	0	0	29.6(4.4)	33.3(8.7)

a: Values represent means of 6 replicates. Blocks were not edge sealed.
b: Values in parentheses are standard deviation.

Table 3.4.2: Average weight losses in OSB after treatment with selected preservatives and exposure to *Gloeophyllum trabeum* in a modified soil-block test[a].

Chemicals	Retention (kg/m^3)		Average weight loss (%)	
	Leached	Unleached	Leached	Unleached
Cu(DMAP)$_2$	3.61	4.26	14.1(3.8[b])	10.7(5.0)
Cu(DMAP)$_2$	2.51	2.01	19.0(5.7)	14.3(2.1)
Cu(DMAP)$_2$	1.29	1.37	38.7(6.2)	31.6(6.0)
ACS	4.32	4.32	33.0(2.0)	3.1(1.3)
ACS	1.95	1.95	43.7(5.0)	13.8(4.2)
ACS	1.02	1.02	62.7(2.1)	40.7(13.6)
CCA	4.03	4.03	23.1(9.9)	22.4(7.3)
Control	0	0	66.5(2.7)	62.5(2.6)

a: Values represent means of 6 replicates. Blocks were not edge sealed.
b: Values in parentheses are standard deviation.

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

A series of experiments were conducted to determine the feasibility of using Cu(DMAP)$_2$ as a wood preservative. The results of these experiments suggest that OSB can be treated by Cu(DMAP)$_2$ in vapor phase, but further study is needed.

Cu(DMAP)$_2$ was synthesized through both alcohol interchange procedure and exchange of sodium alkoxide and a copper tosylate procedure(Chapter II). The exchange approach has some advantages over the interchange although the later produced a higher yield. Theoretically, the exchange method may form a closed loop process that may dramatically reduce the cost, making industrial production of vapor copper possible.

Preservative treatment of OSB using Cu(DMAP)$_2$ applied in the vapor phase was investigated(Chapter III). Treatment time and temperature had a major influence on copper retention and penetration. Complete penetration of OSB was achieved under optimum conditions when treatment time was 80 minutes or longer at 112^{0}C or higher treatment

temperature. Commercial levels of copper retentions were
also obtained.

Tests for the leachability of copper were performed
using a modification of AWPA Standard E-11(Chapter III).
Copper losses in blocks treated to the highest retention
(target retention 4.0kg/m^3 as CuO) were generally lower
with Cu(DMAP)$_2$ than ACS. However, the rate of leaching at
lower retentions(target retention 2.0 and 1.0 kg/m^3 as CuO)
appeared to be slightly higher for Cu(DMAP)$_2$ than for ACS.

The resistance of the treated wafers to
deterioration was assessed using a modified soil block test
on both leached and unleached samples (Chapter III).
Cu(DMAP)$_2$ was slight more effective than ammoniacal copper
sulfate at low retentions in leached samples, but was
slightly less effective than either ammoniacal copper
sulfate or CCA at higher retentions.

RECOMMENDATIONS

Several recommendations for future research could be
made based on the results from this study. The effects of
copper vapor pressure, temperature, treatment time, and
wood moisture content on the penetration and retention of
copper should be studied in selected composites. Also,
other leaching tests such as soil contact exposure should

be performed to develop a better understanding of the stability of vapor copper and studies to determine copper-wood reactions as well. In addition, fungal cellar studies to assess the effectiveness of preservatives should be conducted in order to determine the bioefficacy of $Cu(DMAP)_2$. Finally, it would be interesting to examine the effect of the treatment on the material properties of the composite board.

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