

AN ABSTRACT OF THE THESIS OF

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Title: Limiting Copper Loss from Treated Wood in or Near Aquatic Environments.

Abstract approved:

Jeffrey J. Morrell

Copper migration from treated wood has created concerns within the environmental community because of the potential effects of this heavy metal on aquatic organisms. Migration can be limited, to some extent, by more controlled treatments and by post-treatment processing, but these actions cannot completely overcome the problem. An alternative approach to limit copper migration is to incorporate additives into the formulations that would either block or slow copper loss. Preliminary trials suggest that adding small amounts of Di(hydrogenated tallowalkyl)dimethyl ammonium chloride (2HT), a common fabric softener, to the treating solution can reduce copper losses in service. Reducing copper losses may also allow the use of lower initial preservative loadings. In this research, the potential for using 2HT was examined to reduce copper losses while maintaining preservative efficacy.

The effect of the additive on leaching was assessed by soaking blocks in water over a 14-day period, then examining the resulting leachate. The incorporation of 2HT to alkaline copper-based and DDAC preservative solutions reduced the rate of copper migration from southern pine blocks subjected to laboratory leaching procedures by 5% to 14%. 2HT had no effect on loss rates for isothiazolone. Biological efficacy was assessed by exposing treated blocks to decay fungi in a soil block test. 2HT did not enhance the biological efficacy of copper azole nor isothiazolone in standard laboratory trials with a brown rot fungus, *P. placenta*. The potential for chemical interactions was assessed using Fourier Transform Infrared Spectroscopy (FTIR) analysis. Results indicated that 2HT did not change the structure of wood, suggesting that 2HT reduces copper losses due to ionic interactions between the organic cationic end of the quaternary ammonium compound and the negatively charged surface of wood. This interaction leaves the hydrophobic end of the 2HT exposed to act as a water repellent, thereby excluding the water that would otherwise solubilize and remove copper from the wood. Results provide support for using this additive to limit copper losses into the environment.

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Limiting Copper Loss from Treated Wood in or Near Aquatic Environments

by
June M. Mitsuhashi Gonzalez

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I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

June M. Mitsuhashi Gonzalez, Author

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CONTRIBUTION OF AUTHORS

Dr. Jeffrey J. Morrell assisted with the writing of each manuscript. Dr. Alan Preston and Dr. Lehong Jin were involved with the writing of Chapter 3.

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CHAPTER 1 – INTRODUCTION

Wood preservatives have been widely used to protect wood from decay. Ideally, preservatives should penetrate wood easily, have a long lasting, toxic effect against fungal and insect attack, be harmless to wood and metal, safe to handle, inexpensive, colorless, moisture repelling, clean, odorless, and environmentally friendly, as well as provide a well suited surface for coatings and finishes. No preservative contains all these qualities, although research for developing one continues. The preservatives that have proven to have the best performance against fungal and insect attack at relatively low concentrations are copper-based preservatives, especially chromated copper arsenate (CCA). Copper compounds have been used as biocides for more than one hundred years.

The main disadvantage of copper compounds is their limited fixation to wood. Chromium can help fix soluble copper salts, but there have been increasing environmental issues regarding the carcinogenicity of chromium and arsenic. For this reason, CCA has been withdrawn from residential applications, even though it is considered one of the best preservatives. New copper-based preservatives have been introduced to replace CCA, such as Alkaline Copper Quat (ACQ) and Copper Azole (CuAz). These replacement

systems contain almost twice as much copper as CCA and contain no chromium to aid in copper fixation. Greater amounts of copper are utilized in these preservatives in order to provide sufficient protection against fungi and insect attack, but this increases the amount of copper available for leaching. Organic biocides like isothiazolone and didecyldimethyl ammonium chloride (DDAC) have also been developed as wood preservatives, but none of these systems have proven to be as effective against fungi and insects as copper preservatives.

Concerns about copper migration from treated wood have led to the restrictions on use of this material in or near aquatic environments by some regulators. Leaching of copper, a toxic component that can be harmful to mammals and fish in large quantities, is a problem that environmental regulators wish to limit. One solution to limit leaching would be to coat treated surfaces after installation, but this is uneconomical because surfaces would need constant reapplication. Another approach to limit copper leaching would be to incorporate additives into the preservative formulation that block or slow copper migration.

Preliminary trials performed on 2 x 4 lumber and thick stakes treated with ACQ at different retentions with and without Di(hydrogenated tallowalkyl)dimethyl ammonium chloride (2HT) (Jin et. al., 2006) suggest that

small amounts of this cationic surfactant limited copper migration from treated wood, but the mechanism by which copper movement is affected is unknown. A thorough understanding of how 2HT functions when combined with other preservatives is essential for determining the potential for use of this additive for treating wood.

Literature cited

Jin, L., A.F. Preston, K.J. Archer, F. Cui, A.R. Zahora, and P.J. Walcheski. 2006. Long-chain quaternary ammonium compounds as wood treatment agents. U. S. P. A. Publication. USA, Chemical Specialties, Inc. US 2006/0251915 A1: 11.

CHAPTER 2 – LITERATURE REVIEW

Review of Wood Anatomy and Chemistry

Wood has successfully been utilized as building material for thousands of years due to its availability, ease of use, and great insulating and strength properties. Wood also has some negative aspects, most notable is its susceptibility to degradation. This process of degradation can be inhibited by the addition of preservatives. The potential interactions between wood and these preservative systems can be affected by the composition and structure of wood. Thus, understanding the mechanisms by which these preservative systems perform requires a complete understanding of their structure and chemical composition.

Wood cell walls are composed of three main polymeric materials: cellulose microfibrils, hemicelluloses and an encrusting material, which can be either pectin in the primary cell wall or lignin in the secondary cell wall (Panshin and deZeeuw, 1980). Cellulose forms the structural framework of the cell, making up 40 to 50% of total components in wood. Cellulose is a homopolysaccharide of D-glucose ($C_6H_{10}O_5$)_n held together by a β -(1→4)

glycosidic bond with a degree of polymerization, or number of glucose units in a cellulose molecule, of approximately 10,000 (Sjostrom, 1981) .

Cellulose contains crystalline zones with highly oriented, densely packed cellulose chains (micelle) that make up 65% of the cellulose structure. The crystalline zone is interrupted by amorphous zones of cellulose that are not perfectly aligned and have a lower packed density (Kollmann and Côté, 1968).

Hemicellulose is the matrix substance between the cellulose microfibrils and is composed of heterogeneous branched monosaccharides, whose major components are D-glucose, D-mannose, D-galactose, D-xylose, L-arabinose, L-rhamnose, D-glucuronic acid and 4-O-methyl-D-glucuronic acid.

Hemicellulose has a degree of polymerization of about 200 and makes up 20% to 30% of the dry weight of wood. The amount and type of hemicellulose depends on the kind of wood. The major softwood hemicelluloses are galactoglucomannan (20%) and arabinoglucuronoxylan (5-10%).

Glucuronoxylan (20-35%) is the major hardwood hemicellulose component (Sjostrom, 1981; Saka, 2000). Hemicellulose is often considered to be the component most susceptible to biological degradation because its heteromorphic nature and side chains make it more accessible to enzymatic attack (Curling et. al., 2001; Rowell, 1984).

Lignin is an encrusting, amorphous, hydrophobic polymer that binds wood cells together and is responsible for giving rigidity to the cell wall. Softwoods usually contain 20-30% lignin, while hardwoods contain lesser amounts (18-25%). Softwood lignin is composed of guaiacyl units, while hardwood lignins contain guaiacyl and syringyl units. Lignin is generally considered to be the polymer most resistant to biological degradation (Rowell, 1984).

Cells in wood are composed of two parts: cell wall and lumen. The lumen is the void space inside the cell that allows for water conduction in the living tree. The structure enclosing the lumen, or cell wall, contains three layers: the middle lamella, primary wall, and secondary wall. The middle lamella and primary wall are formed during initial growth of the cell, while the secondary wall is formed during the thickening stage. The secondary cell wall is divided into three sublayers, S1, S2, and S3, based on orientation of the cellulose microfibrils, S3 layer being closest to the cell lumen. The microfibrils in S1 and S3 layers are nearly perpendicular to the length of the cell; while those in the S2 layer run almost parallel to the longitudinal axis. The S1 and S3 layers are thin. S1 layer contains only 40% to 70% polysaccharides, while the S3 layer has the highest cellulose and hemicellulose content, around 85% (Panshin et. al., 1980). The S2 layer is the thickest layer and is, thus,

responsible for most of the physical and mechanical properties of the cell wall. The middle lamella is the layer between the adjacent cells, and this area is often called compound middle lamella due to the difficulty of differentiating the middle lamella from the two primary walls of the adjacent cells (Saka, 2000; Wiedenhoef and Miller, 2005). Although the proportion of lignin in the S2 layer is low compared to S1 and S3 layer, the S2 is the thickest layer and therefore contains most of the lignin in the entire cell wall. Lignin content in the S1 and S3 layers remains relatively constant, at around 15% (Panshin et. al., 1980; Sjoström, 1981).

Cell systems in a tree are oriented in two directions: axial and radial. The axial cell system runs parallel to the length of the tree providing long-distance water movement. In the case of softwoods, these cells are longitudinal tracheids, while hardwoods also contain fibers and vessels. Tracheids, from softwoods, and fibers, from hardwoods, make up more than 80% of wood cells in a tree, and thus are the main contributors to the chemical and physical properties of wood. These cells provide the majority of the mechanical strength of a tree (Wiedenhoef and Miller, 2005). Food storage elements, called longitudinal parenchyma, make up 1-2% of the volume of some softwood species and 0-24% in hardwood species (Kollmann and Côté, 1968; Bowyer et. al., 2003; Hoadley, 1990). Longitudinal parenchyma are relatively short, thin-walled cells and occur in vertical strands that are joined

end-to-end. Some species of wood also contain resin canals, which are tubular intercellular spaces that are surrounded by thin walled-epithelial cells that exude resin into the canal. Resin can help protect against wounds or attack by boring insects (Hoadley, 1990).

The radial system runs perpendicular to the length of the tree, from the pith to the bark. The radial systems of hardwoods and softwoods are composed of ray parenchyma cells that provide lateral transport of biochemicals and storage (Saka, 2000; Wiedenhoef and Miller, 2005) and make up about 7% of the wood volume (Panshin et. al., 1980). Ray parenchyma cells contain more lignin than tracheids, but less cellulose, half the amount of galactoglucomannan, and the same amounts of xylan and pectin than tracheids. Parenchyma cells have a 1,3-linked glucan that is not present in tracheids (Saka, 2000). The ray cells, because of their stored nutrients, are often the initial path for fungal invasion (Zabel and Morrell, 1992). The radial system is also composed of ray tracheids, found only in softwoods. These thick-walled cells constitute the upper or lower margins of rays or may make up the entire ray cells of some conifers (Hoadley, 1990).

The flow of nutrients, water, and gases from cell to cell lumen occurs through openings called pit pairs and perforated plates between adjacent cells. Pits are formed during the development of the cell wall (Panshin et. al.,

1980). Individual pits lack a secondary wall and are internally open to the lumen, with only an external membrane connected to a matching membrane from the other cell (Kollmann and Côté, 1968).

In the case of hardwoods, vessel elements are connected to other vessels through a double end wall that contains perforations. These unrestricted holes facilitate the transport of nutrients, water and gases throughout the length of the tree. The end walls, or perforation plates, develop through the rearrangement of the cell wall material and by enzymes that dissolve portions of the perforation plates (Bowyer et. al., 2003).

Natural Durability of Wood

Over the history of humankind, certain woods have been chosen for building purposes due to their resistance to biological attack. Cedars of Lebanon (*Cedrus libani*) in Jerusalem, teak (*Tectona grandis*) in Babylon and wood from the family *Cupressaceae* in Japan have been used in temples and other wood buildings that date back to the eighth century and continue to resist fungal and insect attack (Hillis, 1987).

Naturally durable wood has been used successfully in a variety of hazardous environments due, in part, to the toxicity of extractives against

biological agents that cause deterioration and due, in part, to a low inherent permeability (Archer and Lebow, 2006). However, durability varies widely between and even within trees of the same species. Roman builders understood this and removed sapwood from logs before use in construction (Hillis, 1987).

The trunk of a living tree is divided into six different layers moving inward: outer bark, inner bark, vascular cambium, sapwood, heartwood, and pith. The outer bark provides mechanical protection to the cambium and prevents water loss. The inner bark, also referred as phloem, conducts sugars, hormones and other nutrients between the leaves and roots. The vascular cambium is responsible for producing inner bark (secondary phloem) to the outside and wood tissue (secondary xylem) to the inside. Sapwood is the active, living wood responsible for conducting water (sap) from roots to leaves. Unlike sapwood, heartwood is dead, nonconductive, and found in the core. Heartwood is often darker-colored and, in some species, contains extractive compounds that lower wood permeability and can limit biological attack (Wiedenhoeft and Miller, 2005).

Extractives are non-structural substances, usually associated with heartwood and exudates that give wood its distinct smell, color and durability properties. Extractive content usually ranges from 2% to 10% by dry weight,

but can represent up to 40% in some species (Rowell et. al., 2005). The classes of extractives found in wood include terpenes and terpenoids, polyphenols, and aliphatic compounds (fats and waxes). These extractives result from a series of chemical processes that occur as the cells in the sapwood gradually senesce. These products are produced at the heartwood boundary (Hillis, 1987; Kozłowski and Pallardy, 1997) and are found in resin canals, epithelial cells and ray parenchyma cells, as well as in the lumen of vessels and tracheids (Sjostrom, 1981). Extractives are so named because they can be removed by solvents without altering the structure of wood (Rowell et. al., 2005).

Heartwood of most species tends to be less permeable than sapwood due to the presence of encrusting materials, such as phenolic compounds, that block bordered pit membranes, the plugging of passages in cells by extractable oils, waxes and gums, or pit aspiration as the torus seals the aperture of the pit canal (Bowyer et. al., 2003). The permeability of the pit membrane depends on its porosity, surface area, and thickness (Hunt and Garratt, 1967). Heartwood permeability can be one to several orders of magnitude lower than sapwood of the same species (Sjostrom, 1981).

Unlike sapwood, which has little natural durability, the heartwood of some species can be highly resistant to insect and fungal attack. Much of this

resistance to biodeterioration is attributed to higher extractive contents of the heartwood (Scheffer and Cowling, 1966; Bamber and Fukazawa 1985; Hillis, 1987), although the concentration of these substances does not always correspond to the degree of natural durability (Kumar and Arganbright, 1980; Hillis, 1987). Heartwood durability reflects reduced permeability, the toxicity of some extractives, the presence of anti-oxidants and some inherent water repellency (Schultz and Nicholas, 2000).

As noted, natural durability varies both within and between trees of the same species. Extractive content can vary significantly among adjacent trees of the same species and even among the growth rings of an individual tree (Taylor et. al., 2003; Taylor et. al., 2006).

Although the use of naturally durable wood is a popular alternative to the use of treated wood, limited availability, concerns about exploitation and deforestation of tropical species, and the variability in durability between and within trees restrict this possibility (Archer and Lebow, 2006). Limited supplies of naturally durable wood have encouraged the use of less durable species that are supplementally protected with preservatives.

Preservation Treatments

A variety of techniques have been developed to protect wood from decay and insect attack. Wood preserving methods are classified as either non-pressure or pressure processes. Non-pressure processes are those that do not use artificial or external pressure and include brushing and spraying, dipping, soaking, steeping, and hot and cold baths. Pressure processes are those in which the wood is placed in a treating cylinder and differential pressure forces are applied to drive the preservative into the wood (Hunt and Garratt, 1967). In general, pressure processes produce deeper, more uniform treatment than non-pressure processes and should produce a longer service life.

Non-Pressure Treatments

Brushing and Spraying

This method is one of the simplest ways to treat wood and can be used for wood that is already in service or at a construction site. The effect of this treatment is superficial and temporary because treatment solution only penetrates a few millimeters into the wood. Under optimal conditions, brushing lengthens service life of a non-durable species by 2 to 3 years (Kollmann and Côté, 1968).

Dipping

This method consists of submerging wood in treating solution for a few seconds to a few minutes. Dipping provides greater coverage and uniformity than brushing or spraying and the solution fills checks in wood. This system extends service life of a non-durable species up to 4 years (Kollmann and Côté, 1968)

Steeping

Steeping consists of immersion of wood in a tank with preservative solution for several days to even weeks. It can be used with both oil and water-based systems, but it was often used with waterborne inorganic salts. Absorption is driven by diffusion of salts from the preservative solution from the water into the timber (Hunt and Garratt, 1967). Penetration and retention levels produced by this process can vary widely (Groenier and Lebow, 2006).

Cold-soaking

This method was mostly used with pentachlorophenol and consists of soaking wood in unheated oil solution. This process may take from 2 days to a week or even longer to produce effective treatment (Hunt and Garratt, 1967). The average service life of cold-soaked treated wood is 16 to 20 years (Groenier and Lebow, 2006).

Hot and cold bath (Thermal Process)

Seasoned wood is submerged for long periods in successive baths of hot and cold preservative solutions. The hot bath expands the air in the external layers of wood and evaporates the surface moisture, while the cold bath contracts the remaining air and vapor in the outer layer, forming a partial vacuum. Atmospheric pressure drives the surrounding solution into the wood. This system is mostly used with coal-tar creosote and oils for treating poles and full-length timbers of durable species (Hunt and Garratt, 1967).

Pressure Treatments

Pressure treatments are the preferred commercial method for protecting wood because the processes are easily managed and controlled and produce a uniformly treated product. Uniform and deeper penetration is achieved in most species as well as greater absorption of preservative than with non-pressure treatments (Kollmann and Côté, 1968).

Full-cell process

The objective of this method is to obtain maximum retention of treating solution in a given zone of treatment. An initial vacuum is applied to remove air from the wood cell, followed by the introduction of preservative solution

without the release of vacuum. Pressure is applied and maintained until the maximum absorption is reached. After the solution has been drained, a final vacuum is applied to recover excess treating solution and reduce dripping. Both oil borne and water borne preservatives can be used with this system (Kollmann and Côté, 1968).

Empty-cell process

Unlike the previous technique, the objective of an empty-cell process is to coat cells with preservative rather than fill them. There are two empty cell processes. One process begins with addition of treating solution at atmospheric pressure, then increases pressure to the desired level. The other process applies a small initial pressure before adding solution. The injection of preservative solution traps the air in the wood. Once the pressure is released, the trapped air expands, forcing the preservative solution out. Finally, a vacuum is applied to remove excess solution (Kollmann and Côté, 1968). These techniques are mainly used with creosote and other oils when treating railway ties, poles, posts, lumber and construction timbers (Hunt and Garratt, 1967).

Chemicals

Wood preservatives have long been used to limit wood decay. Preservatives extend wood service life by introducing toxic chemicals, making the wood resistant to fungal and insect attack. To be suitable for commercial use, wood preservatives should have broad, long-lasting efficacy against wood destroyers, produce no significant negative effects on wood strength, be harmless to wood and metal, have good penetration, uniform retention, be moisture repelling, have low toxicity to non-target organisms, be clean, odorless, and inexpensive. There are two main kinds of preservatives, based on the solvent used to introduce the chemicals into wood structure: oilborne and waterborne.

Oilborne preservatives include creosote, pentachlorophenol and copper naphthenate. These chemicals are mainly used to treat outdoor wood in industrial applications such as railroad ties, timbers, piles, and poles. These preservatives reduce surface checking and provide water repellency. Oilborne preservatives do not react with wood, but are relatively insoluble in water and have low volatility (Hunt and Garratt, 1967; Kollmann and Côté, 1968). Migration of whole oil can be a problem when the treating processes do not

relieve internal pressure adequately, but the primary loss of chemical occurs as water contacts the wood surface, producing slow depletion.

Waterborne preservatives include both metal and organic based systems. Some of the metal systems react with wood, making them resistant to leaching. Organic systems are typically rendered water soluble by adding co-solvents. Once these systems dry, the chemical has low water solubility and resists leaching. Waterborne systems are often preferred because of the clean surface, paintability, lack of odor, low fire hazard and low cost of the solvent. The biggest market for waterborne systems is for residential applications.

The efficacy of waterborne metal preservatives is driven by fixation, where a series of reactions between preservative components and wood components results in the stabilization and insolubilization of toxic elements in wood (Cooper et. al., 1993). Salts formed by elements like copper, chromium, zinc, and arsenic that are contained in preservative solutions react to form insoluble preservative compounds (Hunt and Garratt, 1967).

Copper-based preservatives are the most commonly used waterborne preservatives due to their low cost and efficacy against insect and fungal attack. Copper is broadly toxic to fungi, causing membrane disruption and

inhibiting many important enzymatic reactions. Low levels of copper are less effective against insect attack, although high copper levels are effective against most insects. The reaction sites for copper in wood are the carboxylic groups found in hemicelluloses (Thomason and Pasek, 1997), although Pizzi (1982), Xie et. al. (1995) and Cracium and Kamdem (1997) proposed that copper also complexed with hydroxyl groups from phenolic and carboxylic groups in lignin. Dahlgren (1972) and Pizzi (1982) postulated an ion exchange theory where weak acid groups in wood formed complexes with copper cation by exchanging H^+ .

Chromated Copper Arsenate

The most commonly used waterborne preservative up until January of 2004 was Chromated Copper Arsenate (CCA). CCA was voluntarily withdrawn from residential uses because its arsenic and chromium (VI) components were viewed by the environmental community as unsafe to mammals. Although chromium (VI) is a known carcinogen, it reacts with wood and is reduced to a trivalent state, posing no threat to human health. According to the Best Management Practices for CCA (WWPI, 2006) 99.5% to 99.95% of hexavalent chromium is reduced after completion of wood treatment.

While the general public worries more about arsenic and chromium than about copper, copper is a more serious concern because of the high sensitivity of many aquatic organisms to this metal, especially larval stages of invertebrates. Although copper is a micronutrient at low levels, it can be extremely toxic to some aquatic organisms at concentrations above these levels (Brooks, 1996).

CCA was developed in India in the 1930's (Zabel and Morrell, 1992). At the time, copper was widely used, but most systems tended to leach. The chromium in CCA provided a mechanism for reducing these losses. This fixation markedly improved wood service life. Fixation is a process that reduces the leaching of a preservative component, and is defined by Cooper et. al. (1993) as "the state of chemical components of the preservative wood or other substrate when all chemical reactions are complete". CCA undergoes a series of reactions as hexavalent chromium is reduced to a trivalent state. This reduction simultaneously results in the insolubilization of both arsenic and copper components, providing leaching resistance. Copper is a broad-spectrum fungicide, while arsenic contains insecticidal properties and also protects the wood from copper tolerant fungi. Chromium serves as a corrosion inhibitor and as a fixation agent.

The course of CCA fixation is divided into several phases (Dahlgren, 1975): a momentary initial reaction, a primary precipitation fixation, and a conversion reaction. Most conversion from hexavalent to trivalent chromium occurs during primary precipitation fixation. Four distinct regions have been identified during primary precipitation, each with different fixation rates. Chromium reduction occurs at a higher rate in the first region. During the first and second region, hexavalent chrome undergoes initial ion exchange and adsorption reactions with wood and is fixed as chrome chromate complexes in wood. The fundamental reaction that governs all other fixation reactions occurs in the third region with the fixation of chrome only in a trivalent form. Finally, the last stage consists of fixation of hexavalent chrome as basic chrome chromate. This period concludes when the pH of the wood and the CCA system reach a maximum. At the end of fixation, the final equilibrium fixation products fixed to the wood by ion exchange reaction include CrAsO_4 , Cu(OH)CuAsO_4 , and Cr(OH)_3 .

Anderson (1990) divided CCA fixation into macro-fixation and micro-fixation modes. During macro-fixation, components react promptly in easy-access fluid pathways, creating inorganic precipitates, while also reacting with extractives and readily available cell wall components. In micro-fixation, diffusion of preservative occurs through cell walls, resulting in a variety of inorganic and organic reaction products.

Most of the CCA reacts to form copper chromate or copper arsenate and these products are either complexed with lignin or physically precipitated into cellulose as inorganic salts. The remaining copper reacts with cellulose or lignin as Cu^{2+} , binding to cellulose and in lower amounts as chromate precipitates onto cellulose. The reduction of chromium occurs via reactions with cellulose, while insolubilization results from the reaction of hexavalent chromium with lignin (Pizzi, 1981, 1982).

Fixation can be affected by a variety of wood characteristics including pH, lignin content and extractive level. pH can affect the rates of hexavalent chromium reaction between lignin and cellulose. Wood with higher pH's take longer to complete fixation while those with low pH precipitate more hexavalent chrome early in the fixation process. Lignin content can affect fixation because chromium and copper form more stable complexes with guaiacyl units of lignin in softwoods than with syringyl units present in hardwoods. Polyflavanoid tannin extractives form complexes with metal ions and species with higher extractive levels may fix more rapidly. For example, CCA mixtures precipitate instantly in the presence of flavanoids and lignin at room temperature. The most stable complexes are formed with trivalent chromium and flavanoids. Bivalent copper fixation is nearly as stable as with chromium, while the arsenic fixation rate is much lower (Dahlgren, 1975).

While much has been made of the risks of hexavalent chromium and arsenic, a variety of studies on leachability of wood preservatives have shown that CCA has the greatest resistance to leaching of the various inorganic metallic based systems (Dubey et. al., 2005; Waldron et. al., 2003, 2005). Suttie et. al. (2002) stated that there is no alternative preservative that has shown better results in terms of cost or performance than CCA and that 1.5 times as much copper azole and 3 times as much Alkyl Copper Quat (ACQ) were needed to produce results equivalent to CCA. These higher levels result in much higher copper losses in the absence of a fixative agent such as chromium and it is this lack of strong copper fixation that has raised concerns about the potential environmental impacts of alternative copper systems.

Alkyl Copper Quat / Copper Azole

Despite its excellent performance, CCA was not widely used until the 1970's when the Koppers Company decided to sell CCA treated wood directly to homeowners to meet the demand for durable wood for outdoor living (Connell and Nicholson, 1990). By 1997, CCA represented 97% of the waterborne preservative market (AWPI, 1997). The withdrawal of CCA from residential uses resulted in a shift to alternative wood preservatives like alkyl copper quat (ACQ) and copper azole (CuAz) (AWPI, 1997). Both ACQ and

CuAz differ from acidic CCA in that they use alkaline compounds to solubilize copper.

A 2004 survey of US treating plants showed that ACQ accounted for 41% of waterborne preservatives used, followed by CCA with 35%, and CuAz with 18% (Vlosky, 2004). The fixation of copper in ACQ and CuAz differs markedly from that of CCA and larger amounts of copper must be used in order to attain the same efficacy. ACQ treatments need three times as much copper as CCA and CuAz needs twice as much copper in order to provide equivalent protection against decay and insect attack as CCA (AWPA, 2006d). The large quantity of copper in the alkaline systems, coupled with the limited number of available sites in wood that react with copper (mainly carboxylic groups in lignin and hemicellulose), results in excess mobile copper that remains available for leaching.

ACQ is composed of a copper oxide, a quaternary ammonium compound (quat) that functions as an organic co-biocide, and amines that can complex with and solubilize copper. Unlike CCA, where fixation occurs through an oxidation process forming insoluble copper, chromium and arsenic compounds copper in ACQ fixes by the reaction of amine complexing agents with wood components (Ruddick et. al., 2001), while the quaternary ammonium compounds promote fixation through ion exchange mechanisms

(Archer and Lebow, 2006). The amine component (monoethanolamine) forms donor or sigma bonds with copper (II) in the treatment solution, resulting in a solution with neutral and cationic species (depending on the pH). These copper species form highly stable *bis*-diaminocopper(II) cations that will later complex with phenolic compounds (Ruddick et. al, 2001). Copper fixation begins by the neutralization of acidic groups in wood by the alkali amine system, culminating in the formation of a copper–amine-wood complex along with water insoluble copper complexes (Lucas and Ruddick, 2002). The amine component in the copper amine system forms stable copper-ethanolamine complexes with wood (Jiang and Ruddick, 1999; Ruddick et. al., 2001; Zhang and Kamdem, 2000a). Ethanolamine reacts with C=O groups in COOH groups of hemicellulose as well as with 1,3,4 substituted benzene ring groups in lignin (Humar and Petrie, 2000). This premise is supported by previous research showing that the reactive sites of copper amine fixation reactions are the carboxylic acid functional groups in hemicellulose and phenolic hydroxyl and ester groups in lignin (Thomason and Pasek, 1997; Zhang and Kamdem, 2000b). There is little evidence that copper reacts with cellulose (Lebow and Morrell, 1995), although hydrogen bonds can form between the hydroxyl groups in cellulose and the nitrogen in the amine, resulting in copper-amine-cellulose complexes (Cooper, 1991; Jin and Preston, 1991; Kamdem and Zhang, 2000; Rennie et. al., 1987).

Fixation of amine copper systems is a function of time, temperature, solution concentration (Tascioglu et. al., 2005), wood species and extractive content (Ung and Cooper, 2005). pH differences between the treatment solution and the wood (Habicht and Wittenzellner, 2003), and copper and amine chemistries (Zhang and Kamdem, 2000b) also affect copper complexation. The quantity and nature of copper-amine complexes with wood are affected by the pH of the solution (Druz et. al. 2001). Copper complexes increase at higher solution pH's because acidic wood functional groups are ionized, increasing the number of available reaction sites (Cooper, 1991; Jin and Preston, 1991). Copper fixation also increases as the wood temperature increases, but decreases with increased preservative retention. Preservative retention plays a very important role because cationic amines compete with copper for the same anionic sites in wood, thus higher concentrations of chemical decrease the sites available for selective copper adsorption (Jiang and Ruddick, 2004; Thomason and Pasek, 1997). Increased fixation requires low solution concentrations, but lower retentions will have lower efficacy. It has been estimated that 0.06 to 0.24 mmol of copper per gram of wood may be absorbed when treating wood (Cooper, 1991; Kamdem and Zhang, 2000; Rennie et. al., 1987; Smith and Tascioglu et. al., 2005).

Copper complexes with amine, in the form of monoethanolamine (MEA) ,in treating solutions at a ratio of 1:4 (Kamdem and Zhang, 2000; Mazela et.

al., 2003) but this ratio declines to 1:1 (Jiang and Ruddick, 2004) to 1:1.4 (Lucas and Ruddick, 2002) after leaching. This change occurs because free amine taken up by the cell wall structure in the wood is not strongly bound and is easily removed by leaching. Unfortunately, this excess amine competes with copper and copper-amine bonding to wood (Tascioglu et. al., 2005). Thus, the limited capacity of wood to bind copper at higher retentions (7.9 kg/m^3) results in excessive levels of unreacted copper (Waldron et. al., 2004). This ratio between unreacted amine and copper determines the subsequent leaching resistance of copper and amine complexes in wood (Lucas and Ruddick, 2002).

Initial studies on didecyldimethyl ammonium chloride (DDAC) (Oertel, 1965), the quaternary ammonium compound most commonly used in ACQ, concluded that this compound fixes by an ion exchange mechanism, in which the ammonium cation replaces the proton on the hydroxyl groups present in cellulose chains. However, Preston et. al. (1987) and Tascioglu et. al. (2005) suggested that DDAC fixation to wood occurred through an ion exchange process where the carboxylic acids and phenolic hydroxyls in lignin were the potential reaction sites. Reactivity of DDAC with lignin is much higher than with any other wood component. The adsorption of quaternary compound with wood occurs as follows: lignin>hemicellulose>cellulose. Reactivity of

hemicellulose with the quaternary compound is five times higher than with cellulosic materials (Jin and Preston, 1991).

Copper fixation associated with quats tends to increase with solution pH. The number of available reaction sites increases by the ionization of acidic wood functional groups at higher pH's (Tascioglu et. al, 2005; Jin and Preston, 1991; Cooper, 1991). Copper and ammonium compounds both fix through cationic exchange and ion pairing mechanisms, and the number of available reaction sites is limited. Thus, increasing the treatment solution concentration decreases the degree of fixation (Tascioglu et. al., 2005).

Copper Azole is a preservative formulation that relies on amine copper and an organic azole (tebuconazole) as a co-biocide. Tebuconazole is an insoluble, unleachable, light and heat stable compound that provides protection against copper-tolerant fungi (Grundlinger and Exner, 1990). CuAz functions by altering the structure of hemicellulose, mainly carboxylic groups, reducing the attractiveness of wood to invading organisms (Thomason et. al., 1997).

In general, leaching of components from preservative treated lumber is small, and primarily occurs immediately after the initial exposure of the treated member as unfixed components are removed from the wood surface

(Bergholm, 1992; Evans, 1987). Fixed preservative components can also be leached when in continuous water contact, but this process is slow. Despite their overall low water solubility, components can gradually solubilize in water or the water may contain organic or inorganic components that can either react with fixed preservative material or can change the pH of wood to induce solubilization of fixed products. The result is a gradual release of chemical into the surrounding environment. This can have both environmental and efficacy effects.

Jiang and Ruddick (1999) and Zhang and Kamdem (2000b) suggested that around 9-12% of copper (as CuO) in ACQ treated blocks is lost after leaching with deionized water; however, others have reported losses of 15-22 % and 30 % after 336 hours (Humar et. al., 2003, 2005; Waldron et. al., 2003, 2005). Above ground depletion tests show that 10% of CuO is lost from ACQ treated samples and 9% CuO from CCA samples after 6 months of exposure. Deck tests show that 8-12% of copper leaches from formulations similar to those of CuAz after 20 months of exposure to rainfall, 8-10% copper is lost from ACQ-B decks and only 5% from CCA treated decks (Lebow, 1996). Copper leaching from ACQ on a mass basis has been shown to be two to twenty times higher than from CCA (Archer et. al., 1992; Solo-Gabriele et. al., 2000; Dickey, 2003), while copper losses from CuAz are 3.5 to 17.9 times greater than those of CCA (Dickey, 2003; Hickson Corporation, 1999).

Several models have been developed to predict the rates of metal losses from treated wood exposed in various environments (Brooks, 1998, 2000; Waldron, 2005; Ung et. al., 2005). Brooks' model shows that short-term copper losses from commodity sized ACQ treated wood was predicted to be 8 times higher than from wood treated with CCA and 5 times higher over long-term periods (Brooks, 2000). Waldron (2005) predicted that leaching from the top surface of southern pine decking after one year of being continuously exposed to rainfall would result in loss of about 60% of available copper from ACQ and CuAz treated boards, while CCA leaching would be fairly low.

In addition to higher leaching rates, ACQ and CuAz treated wood accelerate corrosion of metal fasteners, thus only hot-dipped galvanized, copper or stainless steel fasteners and connectors can be used with treated wood.

Organic Preservatives

A variety of organic based alternatives are being assessed as replacements for metal based preservatives, including isothiazolone and DDAC. DDAC is an organic co-biocide in ACQ, but it can also be used as a

stand-alone wood preservative. Leaching tests on DDAC treated dimension material and blocks (Preston et. al., 1987; Ruddick and Sam, 1982) showed that 12-25% of quat leached from wood. This compound is generally not considered to be suitable as a stand-alone wood preservative, although it performs well in mixtures.

Isothiazolones are a group of organic compounds that have shown excellent activity against a range of organisms. These compounds are current used as anti-mold additives in many preservative formulations, but have excellent potential as ground contact preservatives with broad spectrum activity against bacteria, fungi, and termites (Greenley and Hegarty, 1988). 4,5-dichloro-2-n-octyl-4-isothiazolone (RH-287) belongs to this group of compounds and has proven to be very effective against brown rots, white rots, as well as soft rots at very low retentions (Nicholas et. al., 1984). The threshold values obtained from Nicholas' (1984) research suggest a range between 0.37 to 0.50 kg/m³.

Little is known about the reactions between isothiazolone and wood, although the effects on target organisms have been well studied and explained. Isothiazolones are considered to be electrophilic molecules that can rapidly react with thiol groups. The covalent bonded isothiazolone-thiol adducts inactivate a number of fungal enzymes and this physiologically

inhibits respiration, slows growth and causes loss of viability (Chapman et. al., 1998).

Alternatives that Prevent Leaching

Preventing leaching of preservative components from treated wood requires the development of more complete fixation processes. Various methods have been developed to immobilize copper from treated wood, depending upon the preservative involved (WWPI, 2006). These methods include steaming, kiln drying, applying ammonia baths, and more precise treatment schedules. The Best Management Practices (BMP) are a set of treatment and post treatment guidelines that the Western Wood Preservers Institute (WWPI) has implemented to reduce the risk of using treated wood in aquatic and other sensitive environments. Although this guideline ensures better-fixed materials, none of these approaches address leaching issues completely because some copper is always available in the water in the cell lumen. This is especially true immediately after preservative treatment, due to the presence of copper deposits on the wood surface. Thus, initial water exposure produces elevated levels of copper, followed by a rapid decrease to a low, steady leaching rate.

Coating treated wood can be an effective short-term solution for preventing preservative components from leaching, although the coating will wear off and must be reapplied to maintain protection. Among the most common sealants are paint, solid color stains, semi-transparent stains, tinted penetrating finishes, water repellents, varnishes, and natural oil finishes. According to the Forest Products Laboratory (Williams, 1999) service life of these finishes may vary from 1-10 years depending on the product. Semi-transparent stains have been identified as the most efficient coatings to prevent leaching of CCA components for most surfaces, with a service life of 1-2 years (Dickey, 2003; Feist and Ross, 1995). Clear sealers, varnishes, and water repellents provided only limited protection (Dickey, 2003).

An alternative approach to slow copper loss from treated wood would be to incorporate additives in preservative solutions that alter fixation. Additives have been used to enhance the biocidal properties of chemicals and mitigate weathering of treated wood, thereby minimizing the number and depth of checks, while controlling twisting and warping. The ideal additive would be capable of forming a network within the wood structure to fix copper. The compound would have to couple to the wood matrix in addition to carrying groups that can bind copper. Under wet conditions, such compounds would liberate a certain amount of linked copper, allowing it to be soluble and act as

a biocidal agent against fungal or insect attack, but solubility would decrease as moisture content decreased (Roussel et. al., 2000).

The incorporation of additives has proven to be successful in some cases. Combining CCA with a water repellent system minimized the number and depth of checks and helped control warping and twisting of treated lumber (Walcheski and Jin, 2000). Additives have also been used to minimize hardening of CCA treatment to improve climbability of utility poles (Besner et. al., 1999). In addition to enhancing the properties of treated wood, additives can provide protection against the physical effects of weathering produced by the rapid uptake and loss of moisture. These additives can retain surface appearance and, potentially reduce the amount of preservative required for protection (Levi et. al., 1970).

2HT

Di(hydrogenated tallowalkyl)dimethyl ammonium chloride (2HT) (Arquad 2HT-75, Akzo Nobel Inc.) is a common fabric softener. This cationic surfactant is based on a hydrogenated tallow amine ($R_2 - N^+(CH_3)_2 Cl$). The alkyl chain distribution of 2HT consists of mostly long carbon chains (64% C_{18} and 31% C_{16}). 2HT contains a positively charged cationic end is hydrophilic due to the net positive charge of the amine group and a negative anionic end

that is hydrophobic due to the long hydrocarbon radical (Davidson et. al., 1960). Biocidal activity of quaternary ammonium compounds depends on the length of alkyl chains. Short alkyl chains, like those found in DDAC, provide protection against fungi and insect attack. Thus, 2HT has little biocidal efficacy due to the long alkyl chains in its structure (Jin et. al., 2006).

Incorporation of 2HT produced a 75 % reduction in copper losses in a 10-day leaching test on southern yellow pine boards (89x39x305 mm) treated to different ACQ-D retentions. Soil-bed decay tests on ACQ treated stakes with and without 2HT resulted in a 33-50% reduction in copper loss from stakes treated with 2HT after 10 years of exposure (Jin et. al, 2006). These trials suggested that small amounts of 2HT limited copper migration from treated wood, but the mechanism by which copper movement was affected is unknown.

Crutzen (1995) suggested that hydrophobic interactions enable 2HT sorption on cellulose. During dilution, fatty acid chains on the 2HT in contact with water are hydrophobically expelled out of the aqueous phase and deposited onto cellulose through a combination of van der Waals interactions and, to a lesser degree, electrostatic attractions (in the case of negatively charged surfaces). Although 2HT is strongly charged, this charge serves only as a dispersing agent and not as an anchorage (Crutzen, 1995). As a result,

2HT also deposits on charge-free cellulose. Increasing the cellulose surface area in contact with 2HT increases the rate and overall amount of deposition. The organic cationic end balances the negative surface charge in the presence of negatively charged substrates, exposing the hydrophobic end and creating water repellent surfaces (Davidson et. al., 1960). Electrostatic repulsion between absorbed ions by hydrophobic interactions eventually limits 2HT sorption onto cellulose. This process results in a monolayer of 2HT, although negatively charged substrates can form a double layer, thus enhancing water repellency (Ramsbotham, 1989). Ionic interaction forces, based on an electrostatic model, have also been proposed as the driving force in sorption of 2HT on textile surfaces. The affinities between long hydrophobic chains is “above and beyond” that possible from electrostatic interactions (White, 1970), suggesting that other factors contribute to 2HT sorption on cellulosic materials.

The potential mechanisms by which 2HT alters copper losses from wood remain unclear. While improved water repellency could slow wetting and drying cycles, thereby reducing the overall losses, other water repellants have not produced the reductions in copper losses noted with this compound. These results suggest that 2HT may have other, more subtle effects on copper mobility that merits further study.

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**CHAPTER 3 – THE EFFECT OF ADDITIVES ON COPPER LOSSES FROM
ALKALINE COPPER TREATED WOOD**

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Abstract

The replacement of chromated copper arsenate (CCA) as a wood preservative by alkaline copper compounds has heightened awareness of the potential impact of copper losses from treated wood on aquatic organisms. While there remains a healthy debate concerning the actual risk of copper leaching from wood preservatives into aquatic ecosystems, it is clear that reducing these losses will be necessary to avoid continued regulatory actions against the use of preservatives in these environments. Post-treatment processing and coatings can reduce losses, but neither is completely effective. Another alternative is to add compounds to the alkaline system to complex or otherwise reduce copper losses, much in the same way that chromium acts in CCA. One possible additive is Di(hydrogenated tallowalkyl) dimethyl ammonium chloride, also known as 2HT, which is a common fabric softener. Preliminary tests suggested that this compound reduced copper losses from alkaline copper quat and, in doing so, improved overall biological performance. In this report, we describe additional trials to assess the effect of 2HT on copper migration from wood treated with either ACQ or copper azole (CuAz). 2HT had a variable effect on copper migration, but was associated with reduced copper losses in some treatment combinations. Further trials are underway to assess the biological efficacy of wood treated with combinations of 2HT and either ACQ or CuAz.

Introduction

Wood preservatives have been widely used to protect wood from decay. Ideally, preservatives should easily penetrate wood, have a long lasting toxic effect against fungal and insect attack, be harmless to wood and metal, safe to handle, inexpensive, colorless, moisture repelling, clean, odorless, environmentally friendly, as well as provide a well suited surface for coatings and finishes. No preservative has all these qualities, but copper compounds have proven among the best against fungal and insect attack at relatively low concentrations. Copper compounds have been used as biocides for more than one hundred years.

Wood has weak acid groups that complex with copper cations by exchanging H^+ with copper cation (Dahlgren, 1972; Pizzi, 1982 ; Zhang and Kamdem, 2000). The interactions help retain copper in the wood to provide long term protection against biological attack. Wood contains a number of different functional groups with varying dissociation constants (Cooper 1991). The potential bonding sites for copper are primarily hydroxyl groups from phenolic and carboxylic groups (Pizzi, 1982 ; Cracium and Kamdem, 1997).

The main disadvantage of copper compounds is their limited fixation to wood. In the late 1920's, a series of researchers in Germany and later India

explored fixation of copper and settled upon the addition of hexavalent chromium. Chromium undergoes reduction reactions that enhance deposition of soluble copper salts. These results led to the development of chromated copper arsenate (CCA), a preservative that is widely regarded as one of the most effective modern wood preservatives. Despite its efficacy, there have been increasing environmental issues regarding chromium and arsenic toxicity to humans. These issues led to the withdrawal of CCA from the residential use market in North America at the end of 2003. Alkaline copper-based systems have been introduced as arsenic and chromium-free CCA substitutes (Humar and Petrie, 2000). Unlike CCA, which uses chromium to precipitate excess copper and arsenic from the preservative solution, copper fixation in amino-copper preservative systems involves three complex reactions: chemical reactions of the preservative component with hemicellulose and lignin, the formation of amine nitrogen and hydroxyl group complexes that are hydrogen bonded, and the formation of water insoluble salts once the amine has evaporated (Humar and Petrie, 2000). Fixation is directly associated with the number of anionic sites in wood, thus involving cation exchange and ion pair mechanisms. For this reason, amines and copper compete for the same limited number of sites in wood. As a result, fixation, defined as series of reactions that result in the insolubilization of preservative component (Cooper et al., 1993), decreases at increased solution concentrations (Jiang and Ruddick, 1999, 2004; Tascioglu et al., 2005). Compounding this issue is the

need for much higher loadings of copper in alkaline copper systems to produce effective protection. Thus, there are an insufficient number of sites in the wood to adequately fix all of the copper deposited, producing a higher risk of leaching in service

Copper is extremely toxic to many aquatic organisms and concerns about copper migration from treated wood have led to moves by some regulatory bodies to restrict use of copper based biocides in or near aquatic environments. Copper leaching initially begins by loss of unfixated copper at or very close to the surface. Mobile copper is then removed when surface loadings exceed the available fixation sites in wood. Diffusion then transports more mobile copper to the surface as the wood wets and dries, providing a small but steady supply of material for continued leaching. The factors that influence leaching are rainfall (or water exposure), temperature, exposure time and sunlight (Chung and Ruddick, 2004). The greatest preservative losses tend to occur in the period immediately following installation of the member, then decrease with time in service (Brooks, 2000; Waldron et. al., 2005). Copper will always be available to migrate, reflecting the need for some copper to be present in any liquid in the cell lumens to protect against degradation, but the amount required is presumed to be very small and below the minimum effects levels of most non-target organisms (Brooks, 2000).

Coating all treated surfaces after installation would reduce the risk of metal losses, but this process is uneconomical because the surfaces would need constant reapplication to maintain an effective barrier. Alternatively, copper leaching could be reduced by incorporating additives into the preservative formulation that block or slow copper migration. Additives should be hydrophobic and have the ability to react with the wood matrix, easily bond with copper, enable some of the sorbed copper to be released under wet conditions and be able to bind to copper again once the moisture content decreases (Roussel et. al., 2000).

Combining CCA with a water repellent system minimized the number and depth of checks and helped control warping and twisting of treated lumber (Walcheski and Jin, 2000). Water repellants also minimize the inherent hardening effects of CCA treatment (Besner et. al., 1999), and protect against the physical effects of weathering produced by moisture cycling (Levi et. al., 1970). Additives that limit metal loss may also permit the use of lower initial preservative loadings to produce equivalent protection, although this potential would need to be carefully explored in field trials.

Di(hydrogenated tallowalkyl)dimethyl ammonium chloride (2HT) (Arquad 2HT-75, Akzo Nobel Inc.) is a common fabric softener. This cationic surfactant is based on a hydrogenated tallow amine ($R_2 - N^+(CH_3)_2 Cl$). The

alkyl chain distribution of 2HT consists of mostly long carbon chains (64% C₁₈ and 31% C₁₆). 2HT contains a positively charged cationic end is hydrophilic due to the net positive charge of the amine group and a negative anionic end that is hydrophobic due to the long hydrocarbon radical (Davidson, et. al. 1960). Biocidal activity of quaternary ammonium compounds depends on the length of alkyl chains. Short alkyl chains, like those found in DDAC, provide protection against fungi and insect attack. Thus, 2HT has little biocidal efficacy due to the long alkyl chains in its structure (Jin et. al., 2006).

Incorporation of 2HT produced a 75 % reduction in copper losses in a 10-day leaching test on southern yellow pine boards (89x39x305 mm) treated to different ACQ-D retentions. Soil-bed decay tests on ACQ treated stakes with and without 2HT resulted in a 33-50% reduction in copper loss from stakes treated with 2HT after 10 years of exposure (Jin et. al, 2006). These trials suggested that small amounts of 2HT limited copper migration from treated wood, but the mechanism by which copper movement was affected is unknown.

Crutzen (1995) suggested that hydrophobic interactions enable 2HT sorption on cellulose. During dilution, fatty acid chains on the 2HT in contact with water are hydrophobically expelled out of the aqueous phase and deposited onto cellulose through a combination of van der Waals interactions

and, to a lesser degree, electrostatic attractions (in the case of negatively charged surfaces). Although 2HT is strongly charged, this charge serves only as a dispersing agent and not as an anchorage (Crutzen, 1995). As a result, 2HT also deposits on charge-free cellulose. Increasing the cellulose surface area in contact with 2HT increases the rate and overall amount of deposition. The organic cationic end balances the negative surface charge in the presence of negatively charged substrates, exposing the hydrophobic end and creating water repellent surfaces (Davidson, et. al., 1960). Electrostatic repulsion between absorbed ions by hydrophobic interactions eventually limits 2HT sorption onto cellulose. This process results in a monolayer of 2HT, although negatively charged substrates can form a double layer, thus enhancing water repellency (Ramsbotham, 1989). Ionic interaction forces, based on an electrostatic model, have also been proposed as the driving force in sorption of 2HT on textile surfaces. The affinities between long hydrophobic chains is “above and beyond” that possible from electrostatic interactions (White, 1970), suggesting that other factors contribute to 2HT sorption on cellulosic materials.

The potential mechanisms by which 2HT alters copper losses from wood remain unclear. While improved water repellency could slow wetting and drying cycles, thereby reducing the overall losses, other water repellants have not produced the reductions in copper losses noted with this compound.

These results suggest that 2HT may have other, more subtle effects on copper mobility that merits further study.

The ability of 2HT to limit migration of preservative components was assessed using leaching tests on southern yellow pine wood treated with alkyl copper quat, copper azole, DDAC, or isothiazolone at different retentions with and without 2HT

Materials and Methods

Eleven hundred forty four southern yellow pine (*Pinus* spp.) sapwood cubes (19 mm) free of knots and resin pockets per treatment were oven dried (103°C) and weighed prior to being allocated to 44 groups of 26 blocks each. The blocks were then treated to selected retentions of alkaline copper quaternary compound (ACQ), copper azole (CuAz), isothiazolone (ITH) or didecyldimethylammonium chloride (DDAC) using solutions amended with three concentrations of 2HT (Table 3.1). ACQ was formulated with a copper to quaternary ammonium compound ratio of 2:1, while copper azole was formulated using a copper to tebuconazole ratio of 25:1 according to American Wood Preservers' Association Standard P5-04 (AWPA, 2006d).

The blocks were weighted down in beakers containing the respective treatment solution and then subjected to vacuum-pressure impregnation using a treatment cycle consisting of 20 minutes of vacuum (-96 kPa) and 20 minutes of pressure applied at 655kPa. The blocks were left in the solution for an additional 30 minutes before being blotted to remove excess solution and weighed to determine solution uptake. Groups treated with copper-based preservatives were wrapped in plastic for 72 hours and stored at room temperature (20-23°C) to allow any fixation reactions to occur. Samples were then oven-dried and weighed to determine net retention.

Leaching Test

Six treated cubes per group were subjected to a leaching procedure according to AWWA Standard E-11-97 (AWWA, 2006c). The cubes were immersed in 300mL of deionized water that was replaced after 6, 24, 48, 96, 144, 192, 240, 288, and 336 hours. Leachate samples collected at each time point for each treatment group were analyzed for the presence of different preservative components. Copper oxide from CuAz and ACQ leachates was analyzed by ion-coupled plasma spectroscopy (AWWA Standard A21-00) (AWWA, 2004b). Tebuconazole from CuAz leachates was analyzed by high performance liquid chromatography (HPLC) (AWWA Standard A28-01) (AWWA, 2006a) and DDAC from ACQ and DDAC treatments was analyzed by titration (AWWA Standard A16-93) (AWWA, 2004a). Leachates from

isothiazolone treatments were analyzed by HPLC following AWWA Standard A30-00 (AWWA, 2004c)

Preservative retentions in the blocks were determined by grinding six leached and six non-leached blocks to pass a 60 mesh screen. The resulting sawdust was used to assess residual copper by acid digestion of the sawdust and analysis of the resulting solution by ion-coupled plasma spectroscopy (AWWA Standard A21-00) (AWWA, 2004b). Sawdust from CuAz treated blocks was extracted with methanol by sonication and the resulting extract was analyzed for tebuconazole by HPLC according to the AWWA Standard A28-01 (AWWA, 2006a). DDAC was extracted with methanol and analyzed by titration according to AWWA Standard A16-93 (AWWA, 2004a). Isothiazolone was extracted with methanol using an ultrasonic bath and analyzed by HPLC following the AWWA standard A30-00 (AWWA, 2004c). All leachate and sawdust samples were analyzed in the Research and Development laboratory of Chemical Specialties Inc.

The results generated information on copper and DDAC leaching for ACQ with and without 2HT, copper and tebuconazole leaching for CuAz with and without 2HT, DDAC leaching with and without 2HT, and isothiazolone leaching with and without 2HT. The results should be viewed with caution as they represent a limited data base, but they provide a qualitative view of the

effects of 2HT on copper and organic chemical migration. Results from chemical analysis of leachate and sawdust were not statistically analyzed because there was only sample per treatment.

Results and Discussion

Actual retentions for CuAz treated blocks were generally lower than the target levels, but the lowest retentions were still within the range of treatment levels that would be employed in practice (Table 3.2). Actual retentions in ACQ-D treated cubes also tended to exceed the target retention, but the differences were slight, ranging from 0.1 to 1.8 kg/m³ (Table 3.3). The one exception for ACQ was the 0.82 % solution amended with 0.8 % 2HT, which failed to reach the target level; however, the solution employed for this treatment contained slightly less copper than was specified (Table 3.4).

Incorporation of 2HT into CuAz treatments generally reduced leaching rates, although there were some exceptions. For example, copper losses from blocks treated with 0.82 % ACQ solution containing no 2HT were slightly lower than those containing 0.8 % 2HT (Figure 3.1 and Table 3.5). Addition of 2HT to CuAz solutions resulted in consistent reductions in copper losses. For

example, copper losses declined by nearly 2/3 from 18.5 to 6.5 % as 2HT levels increased to 0.8% in a 0.22 % CuAz solution. 2HT tended to produce better results with the highest CuAz treatment and the lowest concentration of 2HT (15% less CuO leached). The addition of 2HT to 0.82% CuAz resulted in higher copper losses than treatments without 2HT.

Although leaching rates (Figure 3.2) obtained by measuring copper oxide loss at various time intervals (6, 24, 48, 96, 144, 192, 240, 288, and 336 hours) did not exactly coincide with those obtained from analyzing sawdust levels of CuO before and after leaching, the overall trends suggest that incorporating 2HT into treatment solutions reduced copper losses. Copper levels in leachates from blocks treated with 0.22% CuAz were minimal whether or not 2HT was added (Figure 3.2A). This suggests that most CuO had reacted with wood at the low concentration and was not available for leaching. The effects of 2HT became more apparent as the concentration of CuAz increased and differences in CuO losses between treatments with and without 2HT became more apparent (Figures 3.2B – 3.2E). The enhanced 2HT effect suggests that increased retentions provided more copper for leaching and this availability was mitigated by incorporation of 2HT.

CuO losses from ACQ-D treated blocks (Figure 3.3 and Table 3.5) were similar to those obtained for CuAz. Copper losses steadily decreased with

increasing 2HT concentration. Copper losses at the highest ACQ concentration (1.22%) with 2HT were lower than those found with the lowest ACQ concentration without 2HT. The results indicate that incorporation of 2HT into ACQ formulations markedly reduces copper losses from treated wood subject to water exposure.

Copper concentrations in leachate from ACQ-D treated blocks were (Figure 3.4). 2HT produced no obvious effect on copper losses from blocks treated with the lowest ACQ-D concentration (Figure 3.4A) probably because most of the copper at that concentration was bound to the available reaction sites in wood (phenolic hydroxyl and carboxylic acid groups in lignin and hemicellulose). Blocks treated with the middle ACQ concentration (Figure 3.4B) experienced a reduction in copper losses in the presence of 2HT, while losses were higher at the highest ACQ concentration (Figure 3.4C).

Leaching of other components such as DDAC from ACQ-D treated wood (Figure 3.5) and tebuconazole from CuAz treated wood (Figure 3.6) also decreased with the addition of 2HT. DDAC experienced 2-4 times less leaching in the presence of 2HT, except for the lowest ACQ-D treatment (0.51%). In general, tebuconazole leaching rates decreased, especially for 0.4% 2HT, but the results must be viewed with caution due to possible surfactant interference with the autotitrator during the analysis.

Incorporation of 2HT into DDAC treatments reduced the amount of DDAC leached (Figure 3.7) from 9% to 13%, except for the 1.22% DDAC treatment with 0.4% 2HT. The results suggest that 2HT not only reduced copper losses but also helped prevent the loss of quaternary ammonium compounds. The rate at which DDAC leached could not be resolved due to the difficulty of differentiating DDAC from 2HT.

Contrary to the results with the copper based preservatives and DDAC, incorporation of 2HT into isothiazolone treatments increased leaching 3 to 6 times (Figure 3.8). Retention analyses of the test blocks suggests that (Table 3.6) this effect was not due to an increased leaching rate, but rather interference of isothiazolone adsorption to wood with addition of 2HT (Figures 3.9 and 3.10). The non-polar isothiazolone was probably out-competed by the strong positive end of 2HT, which limited isothiazolone adsorption to the wood. Clearly, additives such as 2HT must be assessed with each candidate preservative to ensure that they do not adversely affect properties.

Conclusions

Incorporation of 2HT into alkaline copper-based preservative solutions generally reduced copper migration from southern pine blocks subjected to

leaching. The results suggest that additives can alter copper migration in service, producing the potential for reducing environmental concerns and decreasing the amount of copper needed to provide protection against biodeterioration.

The resistance of isothiazolone to leaching was negatively affected by incorporation of 2HT suggesting that 2HT may only be suitable as an additive with certain systems such as metal-based systems or quaternary ammonium compounds.

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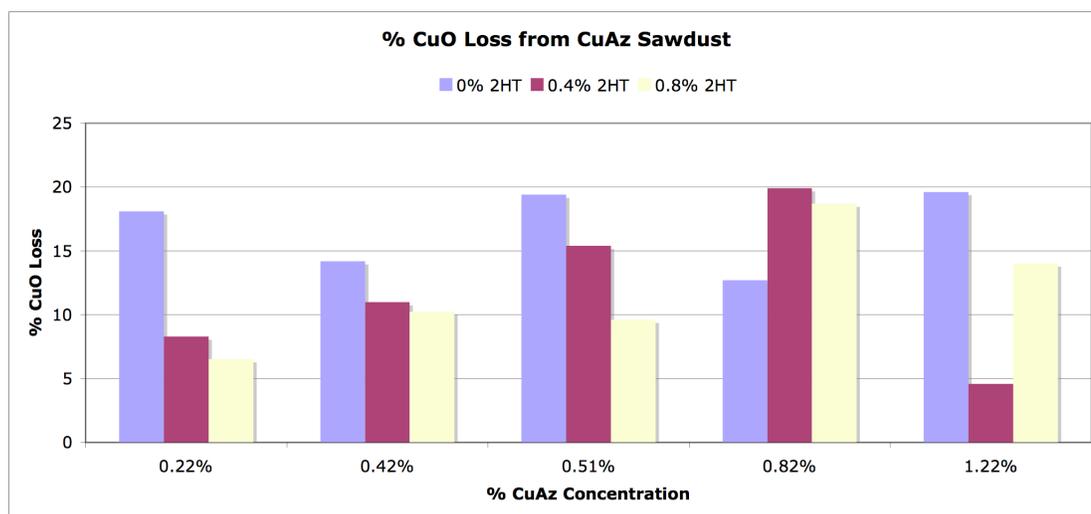


Figure 3.1. Effect of 2HT on CuO losses from southern pine cubes treated with CuAz-B and subjected to an AWP Standard E11 leaching test.

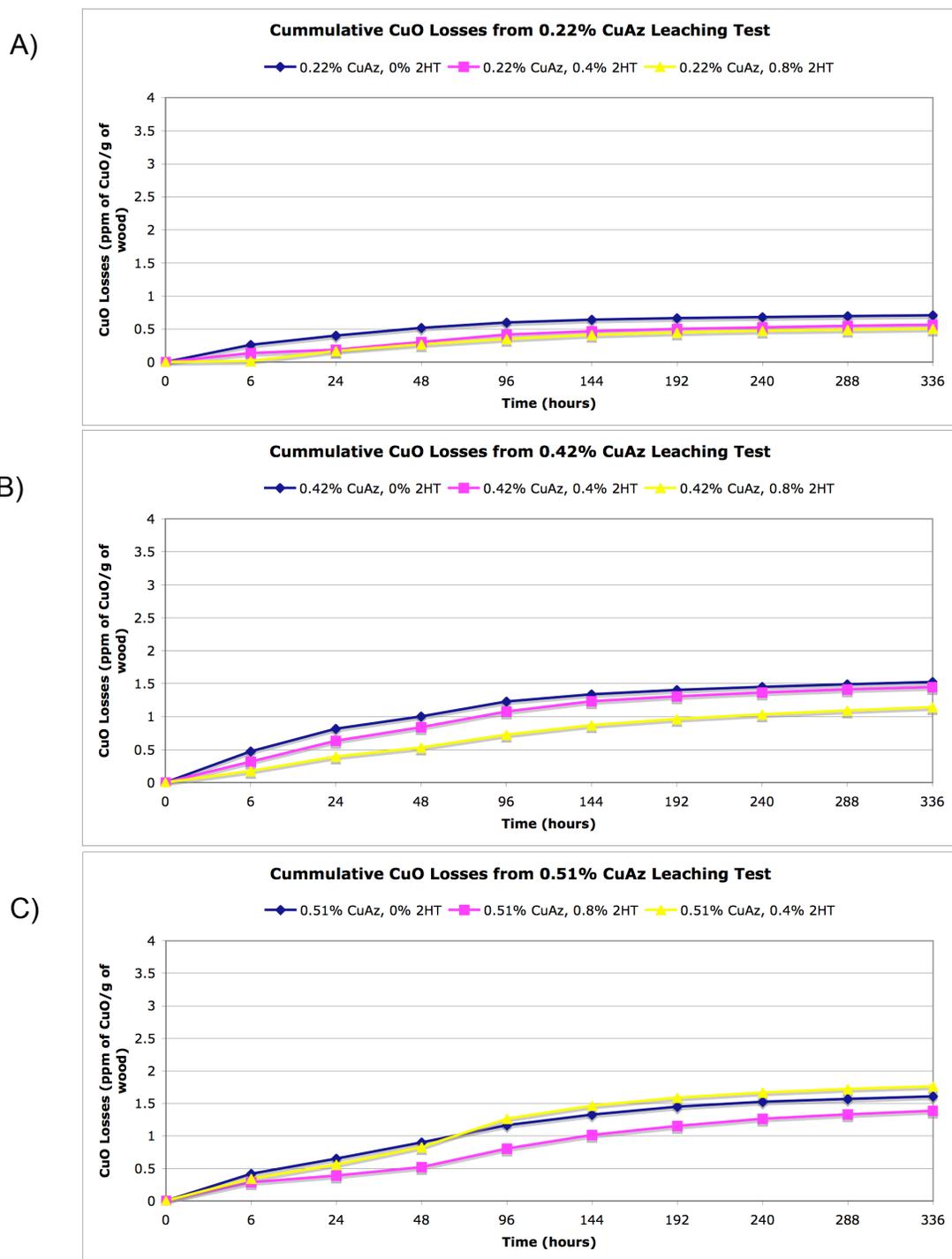
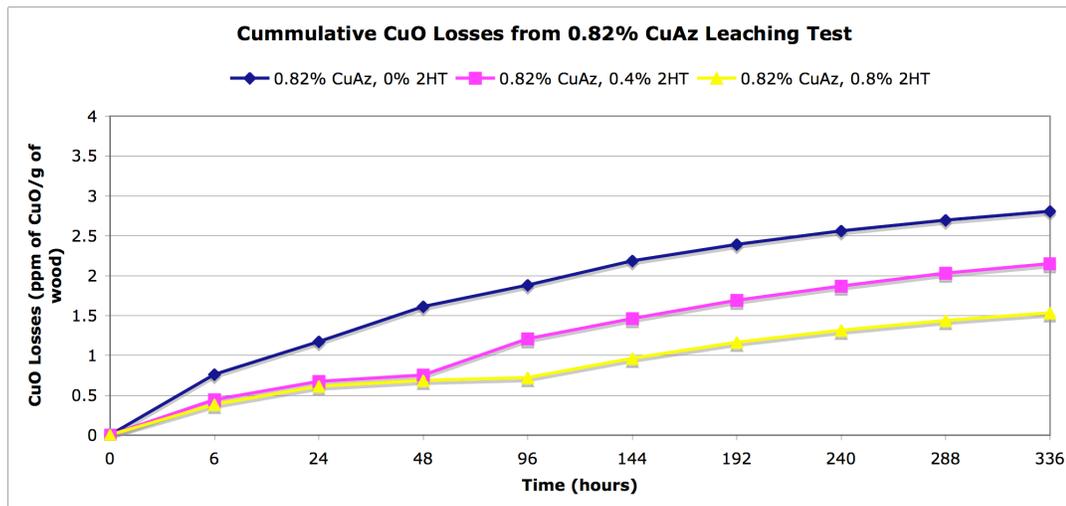


Figure 3.2. Effect of 2HT on cumulative CuO losses from southern pine sapwood blocks treated with CuAz at concentrations of: A) 0.22%, B) 0.42%, and C) 0.51% and exposed to an AWPA Standard E11 leaching test.

D)



E)

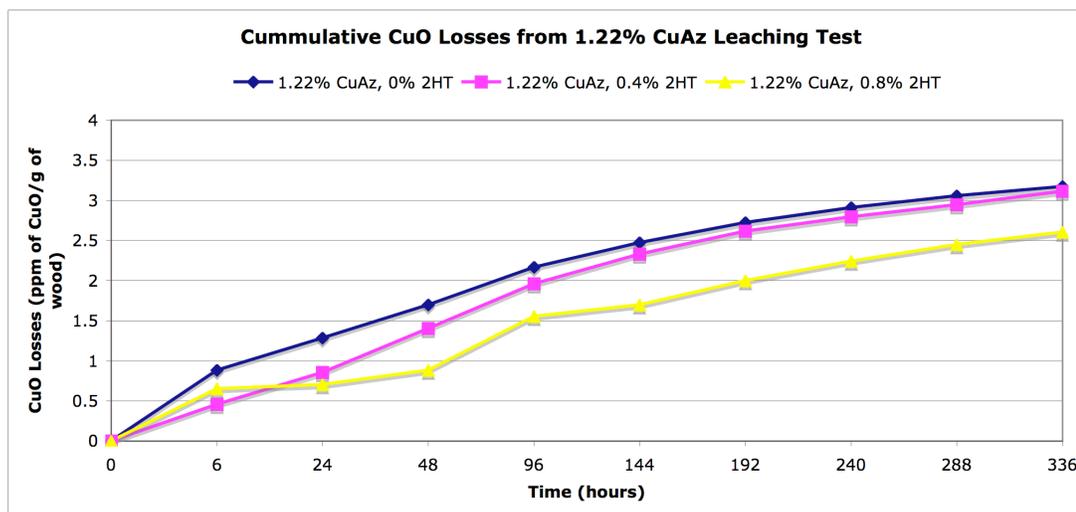


Figure 3.2. (Continued) Effect of 2HT on cumulative CuO losses from southern pine sapwood blocks treated with CuAz at concentrations of: D) 0.82% and E) 1.22% and exposed to an AWPA Standard E11 leaching test.

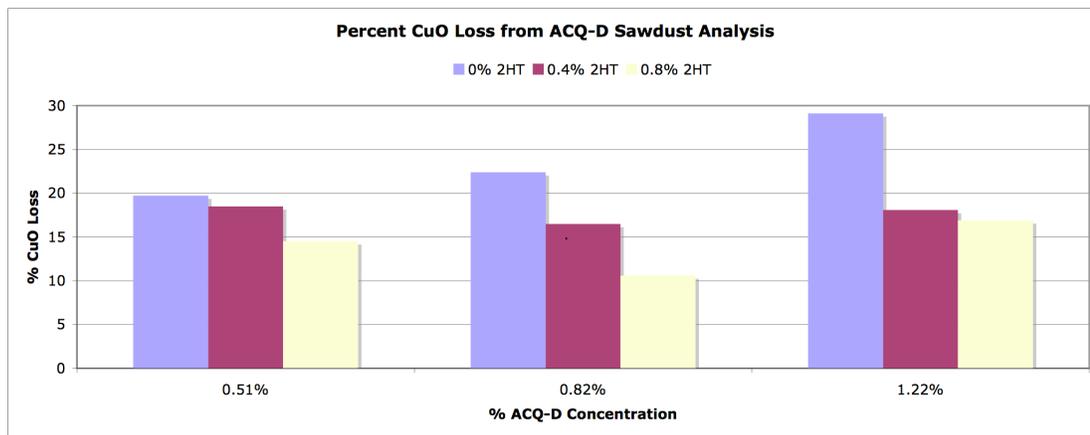
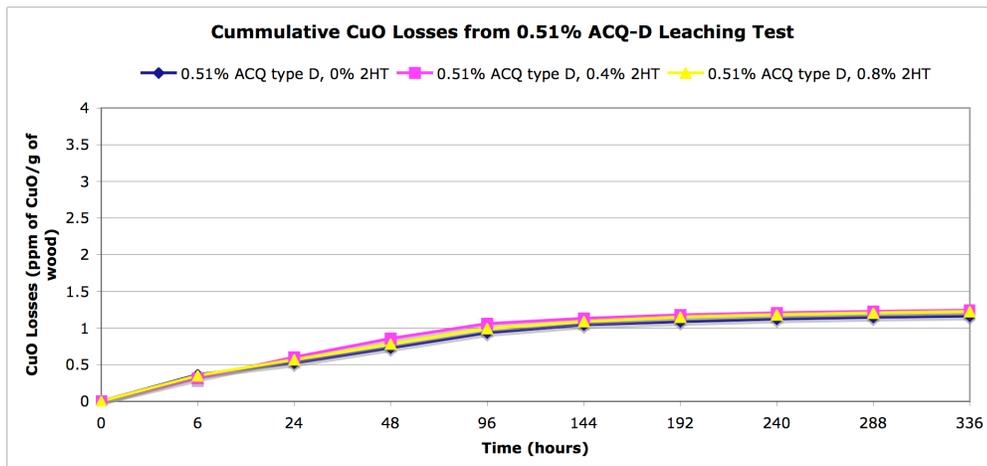
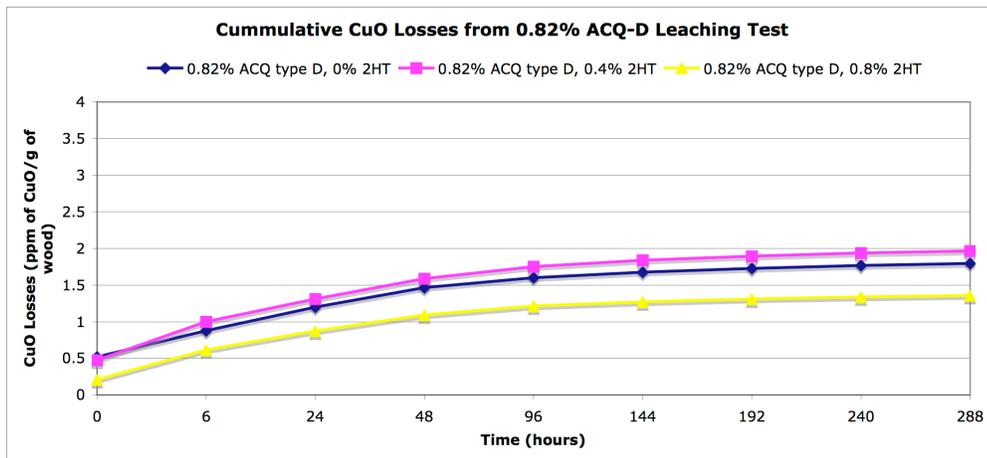


Figure 3.3. Effect of 2HT CuO losses from southern pine cubes treated with ACQ-D and subjected to an AWP Standard E11 leaching test.

A)



B)



C)

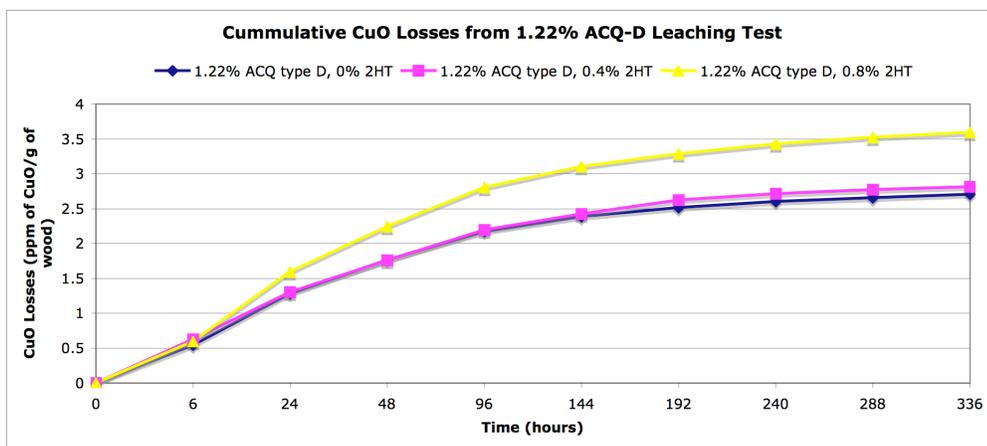


Figure 3.4. Effect of 2HT on cumulative CuO losses from southern pine blocks treated with ACQ-D at concentrations of A) 0.51%, B) 0.82%, and C) 1.22% subjected to an AWPA Standard E11 leaching test.

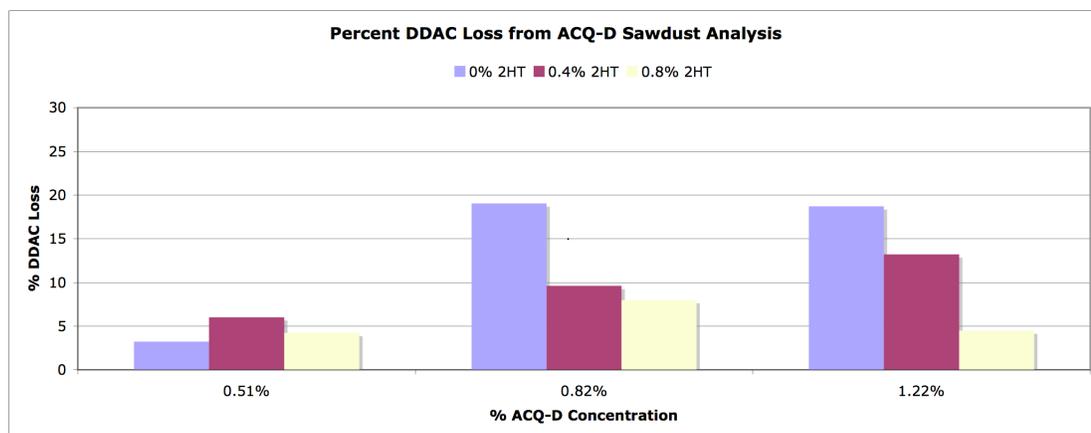


Figure 3.5. Effect of 2HT on DDAC losses from southern pine cubes treated with ACQ-D and subjected to an AWPA Standard E11 leaching test.

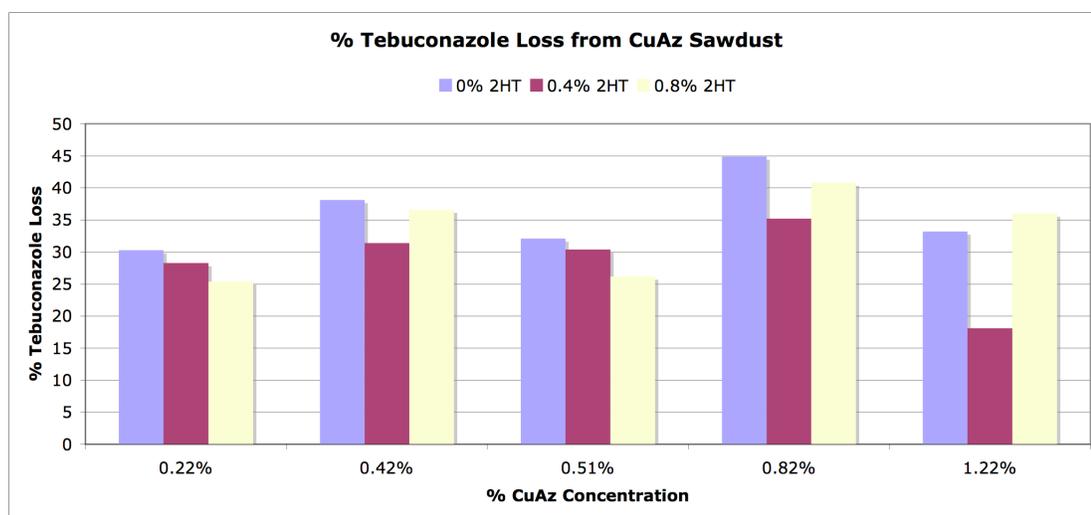


Figure 3.6. Effect of 2HT on Tebuconazole losses from southern pine cubes treated with CuAz and subjected to an AWPA Standard E11 leaching test.

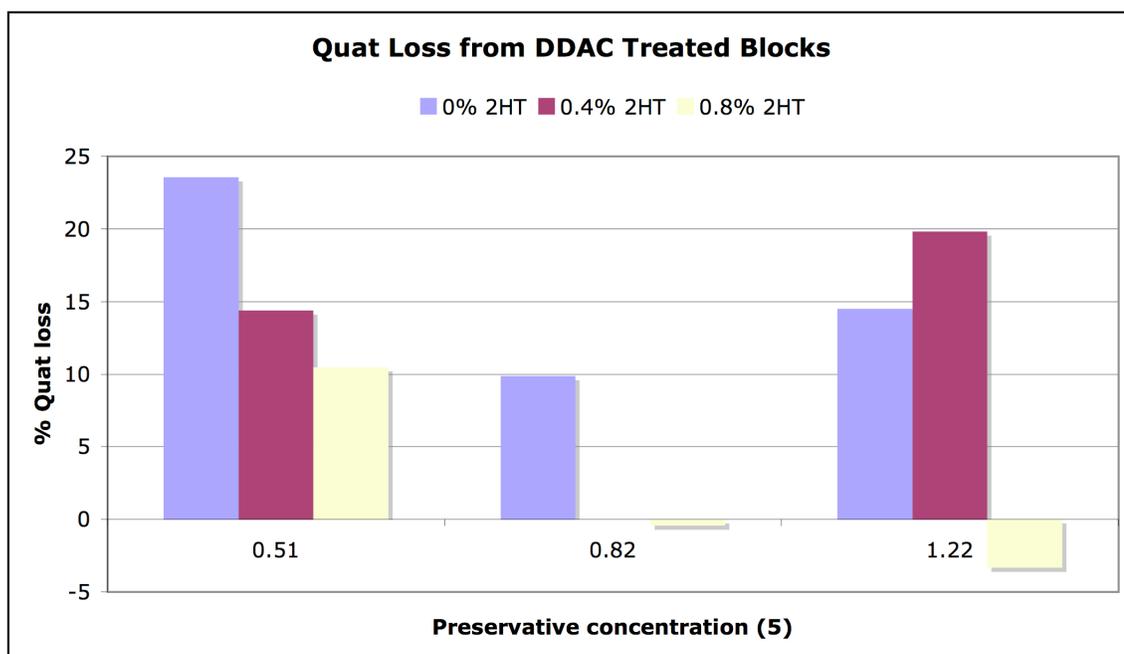


Figure 3.7. Effect of 2HT on losses of quaternary ammonium compounds from from southern pine cubes treated with DDAC and subjected to an AWWA Standard E11 leaching test.

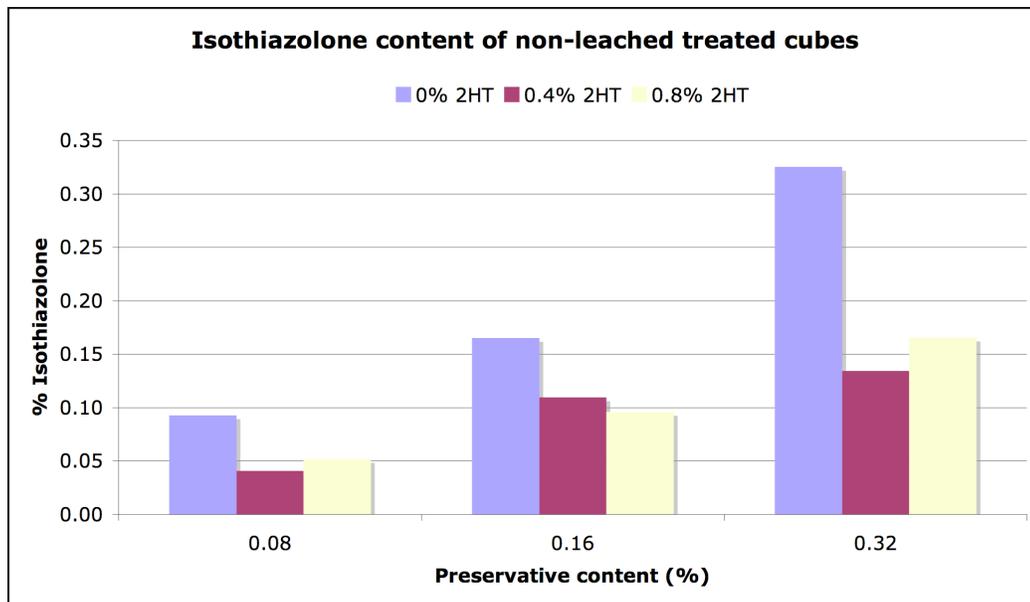


Figure 3.8. Effect of 2HT on isothiazolone losses from southern pine cubes treated with isothiazolone and subjected to an AWP Standard E11 leaching test.

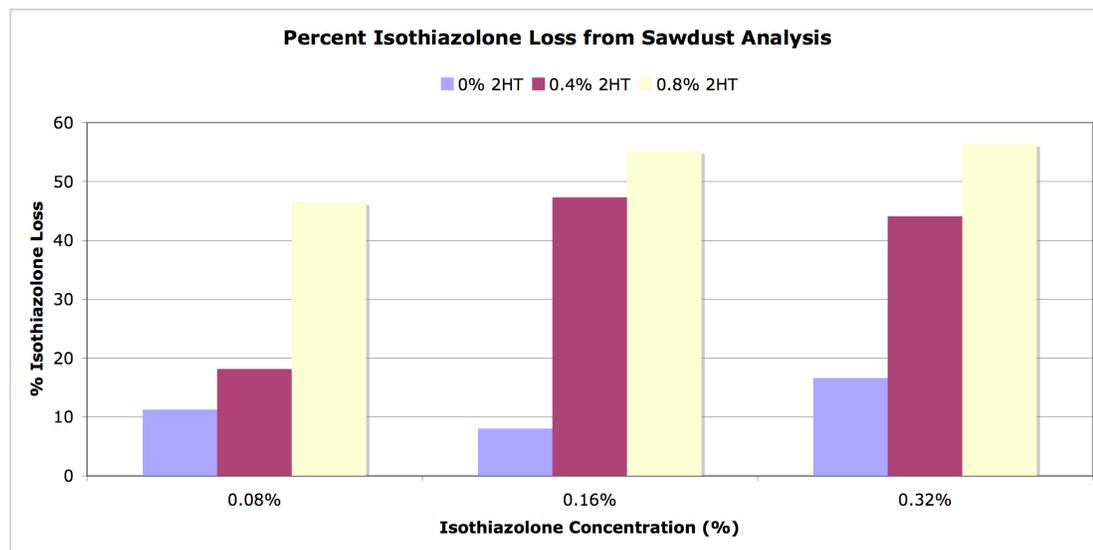


Figure 3.9. Effect of 2HT on uptake of isothiazolone in southern pine blocks subjected to a vacuum/pressure treatment.

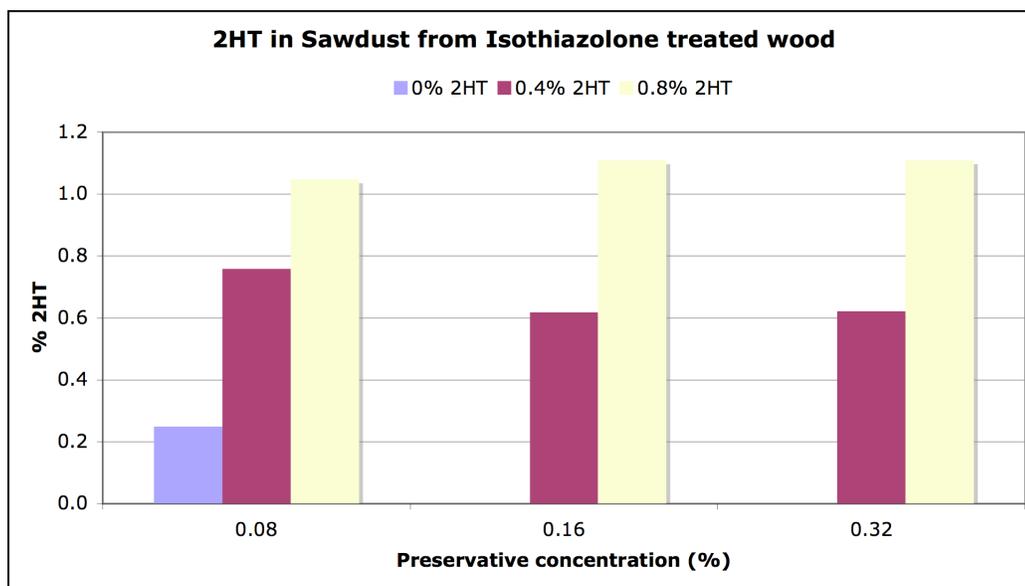


Figure 3.10. Uptakes of 2HT in southern pine blocks treated with various combinations of 2HT and isothiazolone using a vacuum/pressure process.

Preservative	Preservative Concentration (%)		
	2HT Concentration (%)		
	0	0.4	0.8
ACQ	0.51	0.51	0.51
	0.82	0.82	0.82
	1.22	1.22	1.22
CCA	1.22	-	-
DDAC	0.51	0.51	0.51
	0.82	0.82	0.82
	1.22	1.22	1.22
Copper Azole	0.22	0.22	0.22
	0.42	0.42	0.42
	0.51	0.51	0.51
	0.82	0.82	0.82
	1.22	1.22	1.22
Isothiazolone	0.08	0.08	0.08
	0.16	0.16	0.16
	0.32	0.32	0.32

Table 3.1. Treatment combinations used to assess the ability of 2HT to limit preservative leaching in southern pine sapwood cubes (wt/wt in water).

Preservative Type & 2HT (% a.i)	Target CuAz Level (kg/m ³)	Target Cu Level (kg/m ³)	Actual Cu Level (kg/m ³)
0.22% CuAz, 0% 2HT	1.7	1.6	2.0
0.22% CuAz, 0.4% 2HT	1.7	1.6	1.7
0.22% CuAz, 0.8% 2HT	1.7	1.6	1.7
0.42% CuAz, 0% 2HT	3.3	3.2	3.2
0.42% CuAz, 0.4% 2HT	3.3	3.2	3.1
0.42% CuAz, 0.8% 2HT	3.3	3.2	3.0
0.51% CuAz, 0% 2HT	4	3.8	3.4
0.51% CuAz, 0.4% 2HT	4	3.8	3.4
0.51% CuAz, 0.8% 2HT	4	3.8	3.5
0.82% CuAz, 0% 2HT	6.4	6.2	6.4
0.82% CuAz, 0.4% 2HT	6.4	6.2	6.6
0.82% CuAz, 0.8% 2HT	6.4	6.2	5.7
1.22% CuAz, 0% 2HT	9.6	9.2	8.5
1.22% CuAz, 0.4% 2HT	9.6	9.2	8.2
1.22% CuAz, 0.8% 2HT	9.6	9.2	8.5

Table 3.2. Target and actual retentions of CuAz in southern pine sapwood blocks treated with CuAz with and without 2HT using a vacuum/pressure process.

Preservative Type & 2HT (% a.l)	Target ACQ-D Level (kg/m ³)	Target CuO Level (kg/m ³)	Actual CuO Level (kg/m ³)
0.51% ACQ type D, 0% 2HT	4	2.7	3.0
0.51% ACQ type D, 0.4% 2HT	4	2.7	3.1
0.51% ACQ type D, 0.8% 2HT	4	2.7	2.8
0.82% ACQ type D, 0% 2HT	6.4	4.3	4.8
0.82% ACQ type D, 0.4% 2HT	6.4	4.3	4.6
0.82% ACQ type D, 0.8% 2HT	6.4	4.3	3.1
1.22% ACQ type D, 0% 2HT	9.6	6.4	6.8
1.22% ACQ type D, 0.4% 2HT	9.6	6.4	6.7
1.22% ACQ type D, 0.8% 2HT	9.6	6.4	6.9

Table 3.3. Target and actual retentions of ACQ-D in southern pine sapwood blocks treated with ACQ-D with and without 2HT using a vacuum/pressure process.

Preservative Type & 2HT (% a.l)	%CuO in Solution	%Teb in Solution
0.22% CuAz, 0% 2HT	0.256	0.002
0.22% CuAz, 0.4% 2HT	0.261	0.009
0.22% CuAz, 0.8% 2HT	0.257	0.008
0.42% CuAz, 0% 2HT	0.480	0.009
0.42% CuAz, 0.4% 2HT	0.484	
0.42% CuAz, 0.8% 2HT	0.476	
0.51% CuAz, 0% 2HT	0.628	0.004
0.51% CuAz, 0.4% 2HT	0.593	0.013
0.51% CuAz, 0.8% 2HT	0.585	0.019
0.82% CuAz, 0% 2HT	0.97	0.009
0.82% CuAz, 0.4% 2HT	0.947	0.039
0.82% CuAz, 0.8% 2HT	0.941	0.034
1.22% CuAz, 0% 2HT	1.44	0.029
1.22% CuAz, 0.4% 2HT	4.41	0.056
1.22% CuAz, 0.8% 2HT	1.43	0.380

Preservative Type & 2HT (% a.l)	%CuO in Solution	%DDAC in Solution
0.51% ACQ type D, 0% 2HT	0.320	0.153
0.51% ACQ type D, 0.4% 2HT	0.317	0.144
0.51% ACQ type D, 0.8% 2HT	0.33	0.168
0.82% ACQ type D, 0% 2HT	0.506	0.250
0.82% ACQ type D, 0.4% 2HT	0.523	0.251
0.82% ACQ type D, 0.8% 2HT	0.367	0.249
1.22% ACQ type D, 0% 2HT	0.768	0.369
1.22% ACQ type D, 0.4% 2HT	0.763	0.385
1.22% ACQ type D, 0.8% 2HT	0.758	0.380

Table 3.4. Concentrations of ACQ-D and CuAz components in solutions used to treat southern pine sapwood blocks.

Preservative & 2HT Levels	% CuO loss	% Teb loss
0.22% CuAz, 0% 2HT	18.1	30.3
0.22% CuAz, 0.4% 2HT	8.3	28.3
0.22% CuAz, 0.8% 2HT	6.5	25.4
0.42% CuAz, 0% 2HT	14.2	38.1
0.42% CuAz, 0.4% 2HT	11.0	31.4
0.42% CuAz, 0.8% 2HT	10.2	36.6
0.51% CuAz, 0% 2HT	19.4	32.1
0.51% CuAz, 0.4% 2HT	15.4	30.4
0.51% CuAz, 0.8% 2HT	9.6	26.2
0.82% CuAz, 0% 2HT	12.7	44.9
0.82% CuAz, 0.4% 2HT	19.9	35.2
0.82% CuAz, 0.8% 2HT	18.7	40.8
1.22% CuAz, 0% 2HT	19.6	33.2
1.22% CuAz, 0.4% 2HT	4.6	18.1
1.22% CuAz, 0.8% 2HT	14.0	36.0

Preservative & 2HT Levels	% CuO loss	% DDAC loss
0.51% ACQ type D, 0% 2HT	19.7	3.2
0.51% ACQ type D, 0.4% 2HT	18.5	6.0
0.51% ACQ type D, 0.8% 2HT	14.5	4.3
0.82% ACQ type D, 0% 2HT	22.4	19.0
0.82% ACQ type D, 0.4% 2HT	16.5	9.6
0.82% ACQ type D, 0.8% 2HT	10.6	8.0
1.22% ACQ type D, 0% 2HT	29.1	18.7
1.22% ACQ type D, 0.4% 2HT	18.1	13.2
1.22% ACQ type D, 0.8% 2HT	16.9	4.5

Table 3.5. Effect of 2HT on losses of various preservative components from southern pine sapwood blocks treated with ACQ-D or CuAz and subjected to an AWP Standard E11 leaching procedure.

**CHAPTER 4 - THE EFFECT OF ADDITIVES TO LIMIT FUNGAL ATTACK
ON WOOD TREATED WITH VARIOUS WOOD PRESERVATIVES**

June Mitsuhashi

Jeffrey J. Morrell

Abstract

Most wood preservatives have limited water solubility that results in some chemical always being available when the wood is wetted, and thus at a risk of decay. This solubilized chemical can migrate from the wood over time, thereby reducing the degree of protection against biological attack and potentially affecting non-target organisms away from the wood. Incorporating additives into preservative formulations could help limit leaching of preservative components from treated wood. The ability of one potential additive, Di(hydrogenated tallowalkyl)dimethyl ammonium chloride (2HT), to inhibit preservative migration and thereby enhance biological activity was evaluated on Southern yellow pine blocks were treated with various wood preservatives (alkyl copper quat, copper azole, DDAC, and isothiazolone) with and without 2HT. Treated blocks were exposed to a brown-rot fungus (*Postia placenta*) in a soil block test following procedures described in AWWA Standard E-10-01 to determine whether 2HT incorporation enhanced resistance to fungal attack. 2HT had no significant effect on decay resistance of blocks treated with copper-based or organic preservatives, demonstrating that 2HT did not appear to improve the biological efficacy of any of the preservative formulations evaluated.

Introduction

Wood has successfully been utilized as building material for thousands of years due to its availability, ease of use, and great insulating and strength properties. Wood also has some negative aspects, most notably is its susceptibility to degradation. Biodeterioration is the main cause of failure of wood in service, and fungi are the primary agents of biodeterioration in most environments.

Fungi, like all living organisms, need water, oxygen, favorable temperature and pH, and a source of food (wood) for their growth and development (Zabel and Morrell, 1992). While moisture control is the primary approach to wood protection in most applications, it is not always possible to limit wetting. In these instances, altering the substrate through addition of chemicals that are toxic or inhibitory to decay agents has long been an accepted approach for enhancing wood performance.

Copper based preservatives have long been used to limit wood decay. These preservatives extend wood service life by making the wood resistant to fungal and insect attack. To be suitable for commercial use, wood preservatives should have broad and long-lasting efficacy against wood destroyers, produce no significant negative effects on wood strength, be

harmless to wood and metal, have good penetration, attain uniform retention, be moisture repelling, have low toxicity to non-target organisms, be clean, odorless, and inexpensive. No preservative meets all these requirements, but there are continuing efforts to develop safer systems for wood protection.

Decay hazards increase markedly when wood is exposed to ground contact and periodic wetting. All preservative have some degree of water solubility and it is this solubility that allows some level of chemical to be present in the wood cell lumens to act upon agents of decay that may attack the wood. As a result of this low level solubility, preservative components exposed under moist conditions can leach from the treated wood, resulting in a gradual release of chemical into the surrounding environment. This migration has two consequences. It has the potential to negatively affect non-target organisms, but it can also reduce the residual loadings in the wood leaving the wood susceptible to decay.

Coating treated wood can be an effective short-term solution for preventing preservative components from leaching, although coatings wear off and must be reapplied regularly to maintain the protection. Among the most common sealants are paint, solid color stains, semi-transparent stains, tinted penetrating finishes, water repellents, varnishes, and natural oil finishes. All of these systems will work to some extent, but all degrade over time (Dickey,

2003). In some instances, degraded coatings can increase the risk of decay because they retain moisture, thereby prolonging conditions suitable for fungal attack.

An alternative approach to slow copper loss from treated wood could be the incorporation of additives in preservative solutions. Additives are commonly incorporated into preservative systems to enhance the biocidal properties of chemicals mitigate weathering of treated wood, minimize checking and help control twisting and warping of treated wood (Walcheski and Jin, 2000; Besner et. al., 1999; Levi et. al., 1970). The ideal anti-leaching additive would form a network within the wood structure to fix copper. Compounds would have to couple to the wood matrix in addition to carrying groups that can bind copper. Under wet conditions, the compound would liberate small amounts of soluble copper that would act as a biocidal agent against fungal or insect attack. The copper would then be resorbed once the moisture content decreases (Roussel et. al., 2000). At present, no such compound is available, but a fixative method would help mitigate concerns about copper migration into the environment. It might also improve the biological performance of copper based systems by slowing copper losses and thereby maintaining threshold levels of copper in wood for longer periods of time. This might also allow for the use of lower copper loadings to produce equivalent biological performance

Preliminary trials using Di(hydrogenated tallowalkyl)dimethyl ammonium chloride (2HT) (Arquad 2HT-75, Akzo Nobel Inc.), a common fabric softener, suggested that small amounts of this compound limited copper migration from treated wood (Jin et. al., 2006). 2HT is a cationic surfactant based on a hydrogenated tallow amine ($R_2 - N^+(CH_3)_2 Cl$). The alkyl chain distribution of 2HT consists of mostly long carbon chains (64% C_{18} and 31% C_{16}). 2HT contains one negatively charged anionic end that is hydrophobic due to the long hydrocarbon chain and a positively charged cationic end that is hydrophilic due to the net positive charge of the amine group (Davidson et. al., 1960). In addition, this compound is readily available, inexpensive and has relatively little toxicity.

A soil-bed decay test performed on ACQ treated stakes with and without 2HT showed that addition of 2HT produced a 33-50% decrease in copper losses after 10 years of exposure (Jin et. al, 2006). These trials suggested that small amounts of 2HT limit copper migration from treated wood.

The objective of this study was to evaluate the effects of 2HT on the performance of various wood preservatives in standard laboratory decay tests.

Materials and Methods

The overall approach was to assess the effects of 2HT on decay resistance using small southern pine sapwood cubes treated to various retentions with the desired wood preservatives and then exposing these blocks to fungal attack in a soil block test.

Block Treatment

Southern pine sapwood blocks (*Pinus* spp.) (19 mm cubes) were oven dried (103°C) and weighed prior to being allocated into groups of 14 blocks per treatment. Blocks were treated with alkaline copper quaternary compound (ACQ)(2:1 copper: didecyldimethylammonium chloride), copper azole (CuAz)(25:1 copper:tebuconazole), isothiazolone (ITH) or didecyldimethylammonium chloride (DDAC) with or without one of three concentrations of 2HT (Table 4.1). Preservative systems were prepared according to American Wood Preservers' Association Standard P5-04 (AWPA, 2006d). For treatments that contained 2HT water was heated to 50°C to allow the additive to dissolve and the preservative formulation was then added to the mixture at the desired level.

Preservative	Preservative Concentration (%)		
	2HT Concentration (%)		
	0	0.4	0.8
ACQ	0.51	0.51	0.51
	0.82	0.82	0.82
	1.22	1.22	1.22
CCA	1.22	-	-
DDAC	0.51	0.51	0.51
	0.82	0.82	0.82
	1.22	1.22	1.22
Copper Azole	0.22	0.22	0.22
	0.42	0.42	0.42
	0.51	0.51	0.51
	0.82	0.82	0.82
	1.22	1.22	1.22
Isothiazolone	0.08	0.08	0.08
	0.16	0.16	0.16
	0.32	0.32	0.32

Table 4.1. Treatment combinations used to assess the ability of 2HT to limit brown-rot decay (*P. placenta*) in southern pine sapwood cubes (wt/wt in water).

The blocks were submerged in a container with the respective treatment solution, then subjected to a 20 minute vacuum (-96 kPa) followed by 20 minutes of pressure (655 kPa). The blocks were left in solution for an additional 30 minutes, then removed, blotted to remove excess solution and weighed. Weight gain was used to calculate net solution absorption. The blocks were then wrapped in plastic and stored for 72 hr at 20 to 23°C to permit any wood/preservative reactions to proceed. The blocks were then oven-dried (103 C) and weighed.

Six blocks per treatment were leached following the procedures described in AWWA Standard E-11-97 (AWWA, 2006c) where cubes were immersed in 300 mL of deionized water that was replaced after 6, 24, 48, 96, 144, 192, 240, 288, and 336 hours. Leachate from each time point was retained as part of a separate trial to assess the effects of 2 HT on preservative migration.

Soil Block Tests

The decay resistance of treated and non-treated blocks was assessed using AWWA Standard E10-01) Standard method of testing wood preservatives by laboratory soil-block cultures (AWWA, 2006b). Decay chambers were prepared by half filling 454 ml glass French squares with moist loam, adding a western hemlock (*Tsuga heterophylla* (Raf) Sarg) feeder square (3mm x 28mm x 34 mm) and then adding moisture to the desired level. The bottles were then loosely capped and sterilized by autoclaving for 30 minutes at 121°C. After cooling, an agar disc cut from the edge of an actively growing culture of *Postia placenta* (Fr.) Larsen et Lombard (Isolate Madison 698) was placed on the corner of the feeder square, and then the bottles were incubated for 7 to 14 days until the fungus had completely covered the feeder strip. This fungus was chosen because of its well-known tolerance of copper based biocides.

Eight non-leached, six leached blocks from each treatment (Table 4.1) and two control (non-treated) blocks were sterilized by exposure to 2.5 MRads of ionizing radiation from a cobalt 60 source. Six leached, six non-leached and two control blocks were then introduced into decay chambers (2 per chamber). The remaining two blocks from each treatment were introduced into sterile chambers. All bottles were incubated at 28°C and 80% relative humidity for 12 weeks. At the end of the exposure period, the blocks were removed from the chambers, scraped clean of fungal mycelium and weighed to determine wood moisture content. The blocks were then oven dried (103°C) and weighed to determine wood weight loss over the exposure period. The mean weight loss of the two blocks in non-inoculated chambers was subtracted from the weight of non-leached blocks to account for any preservative components or wood extractives that might have leached from the wood into the feeder strip due to the high moisture content in the chamber.

Weight loss data were subjected to an Analysis of Variance using the program S Plus to assess the effect of additive on wood weight loss. Differences between means were then assessed using Tukey's Least Significant Difference Test at a 0.05 level.

Results and Discussion

Actual retentions for CuAz treated blocks were generally lower than the target levels, but the lowest retentions were still within the range of treatment levels that would be employed in practice (Table 4.2). Actual retentions in ACQ-D treated cubes also tended to exceed the target retention, but the differences were slight, ranging from 0.1 to 1.8 kg/m³ (Table 4.2). The one exception for ACQ was the 0.82 % solution amended with 0.8 % 2HT, which failed to reach the target level; however, the solution employed for this treatment contained slightly less copper than was specified (Table 4.2). Actual retentions for isothiazolone without 2HT were slightly lower but once 2HT was incorporated isothiazolone levels plummeted, suggesting 2HT obstructed isothiazolone from adsorbing to wood (Table 4.3). DDAC actual levels were much higher than the target due to inability to separate the quaternary ammonium compounds, DDAC and 2HT (Table 4.3).

Weight losses of untreated control blocks averaged 47.8%, which indicated that conditions were suitable for aggressive fungal attack. Weight losses for all chemically treated blocks tended to be extremely low in comparison with the non-treated control. Weight losses for CCA treated cubes averaged 0.56% for the non-leached blocks and 1.06% for the leached blocks, illustrating the excellent protection afforded by this system. None of the

leached treatments (ACQ, CuAz, DDAC, ITH), with or without 2HT, had lower or equivalent weight losses than CCA leached blocks.

Weight losses of non-leached CuAz treated cubes were generally less than 1% (Figure 4.1 and Table 4.4). Weight losses for leached CuAz treated blocks were 2 to 15 times higher than those for comparable non-leached samples even when 2HT was present (Figure 4.2 and Table 4.5). Furthermore, there was no consistent dose response pattern; increasing CuAz concentrations did not increase protection against *P. placenta*. The incorporation of 2HT into CuAz treatments produced no significant improvement in decay resistance (two sided p-value = 0.15 from a multiple linear regression) (Tables 4.5 and 4.6). The results indicate that 2HT does not markedly alter the performance of CuAz treated wood.

Weight losses of non-leached ACQ treated blocks were comparable to those obtained with CCA or CuAz treated wood (~0.5-1%) (Figure 4.3 and Table 4.7). Weight losses in leached blocks were lower than for CuAz leached blocks, but 2 to 5 times higher than those found on CCA leached blocks (Figure 4.6). Chromium has a profound influence on copper mobility and these results highlight the effects of the lack of an immobilization agent. As with CuAz treatments, 2HT did not significantly affect ACQ performance against brown-rot attack (two sided p-value = 0.526 from a multiple linear

regression (Table 4.8 and 4.9) and there was no consistent dose response pattern.

In both alkaline copper treatments, there was tendency towards higher weight losses with increasing treatment levels on both leached and non-leached blocks. This trend reflects increasing levels of copper available for leaching rather than a reverse dose effect.

Weight losses of non-leached DDAC treated blocks were also less than 1% (Figure 4.5 and Table 4.10). Weight losses of leached blocks were lower than those obtained on blocks treated with copper based preservatives, including CCA. DDAC was the most effective preservative against *P. placenta* attack, which is not surprising considering that this fungus is copper tolerant. As with the previous preservative systems, incorporation of 2HT into DDAC did not produce a significant improvement in decay resistance (two sided p-value = 0.1792 from a multiple linear regression) (Table 4.11 and 4.12).

Non-leached isothiazolone treated blocks experienced little or no weight losses when treated with 0.16 or 0.32 % isothiazolone but weight losses on blocks treated with the lowest isothiazolone concentration were above the background level (Figure 4.7 and Table 4.13). The results suggest that the threshold value for this chemical against *P. placenta* lies between 0.08% and

0.16%. Weight losses in leached isothiazolone blocks ranged from 2-9% (Figure 4.8 and Table 4.13) compared to non-leached cubes, suggesting that the chemical was susceptible to leaching, although the weight losses were still relatively low. 2HT had no significant effect on isothiazolone performance against *P. placenta* (two sided p-value = 0.4428 from a multiple linear regression) (Table 4.14 and 4.15). Isothiazolone treatment did tend to make the wood more susceptible to darkening during over drying, suggesting that heating degraded the wood and some cubes were removed from the analysis for this reason.

2HT was hypothesized to enhance performance of copper-based biocides by reducing copper losses, thereby prolonging the time when the copper levels remained effective for fungal protection. The results suggest that 2HT did not enhance the activity of any of the systems evaluated against *P. placenta*; however, the weight losses tended to be low for all treatments. It might be useful to examine the effects of 2HT on the performance of these same compounds against other decay fungi either alone or in a fungal cellar where the wood can be exposed to a range of decay organisms.

Conclusions

2HT did not appear to enhance the biological efficacy of either CuAz, ACQ, DDAC or isothiazolone in standard laboratory trials at the levels tested.

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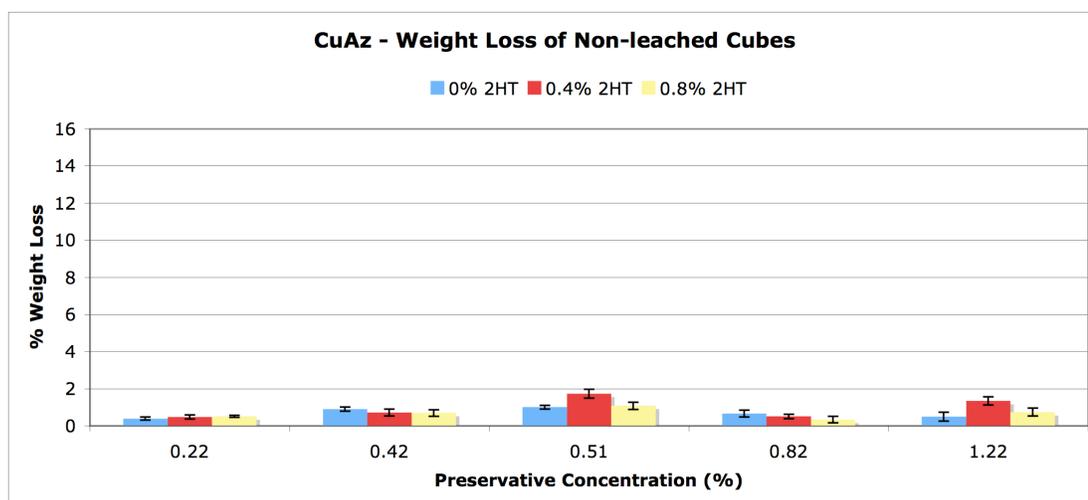


Figure 4.1. Effect of 2HT on resistance of non-leached copper azole treated southern pine sapwood blocks to attack by *Postia placenta* in a soil block test.

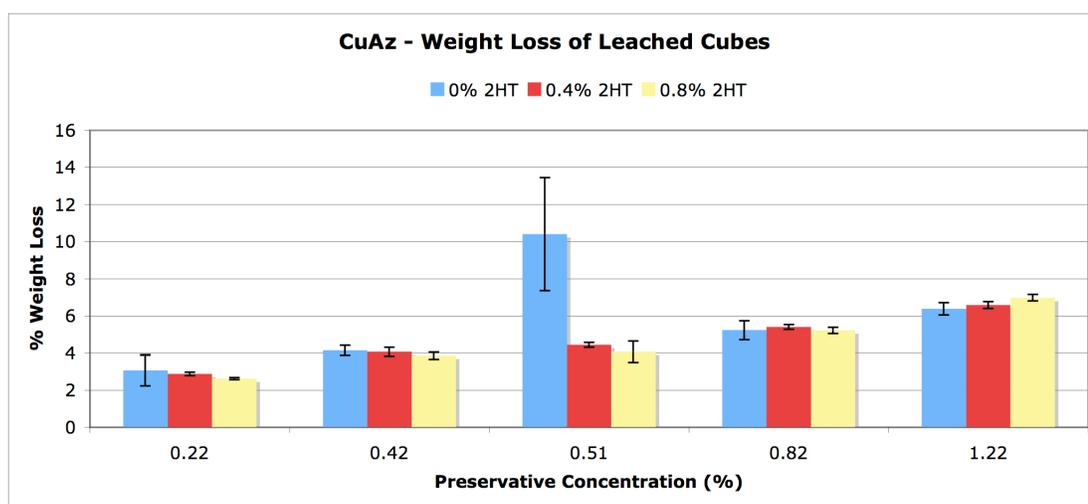


Figure 4.2. Effect of 2HT on resistance of leached copper azole treated southern pine sapwood blocks to attack by *Postia placenta* in a soil block test.

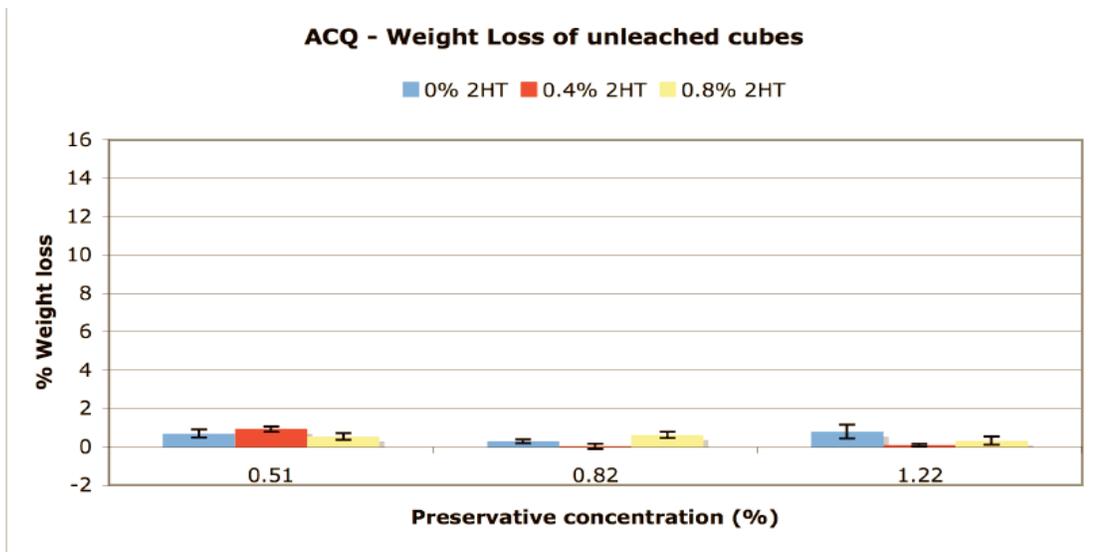


Figure 4.3. Effect of 2HT on resistance of non-leached ACQ treated southern pine sapwood blocks to attack by *Postia placenta* in a soil block test.

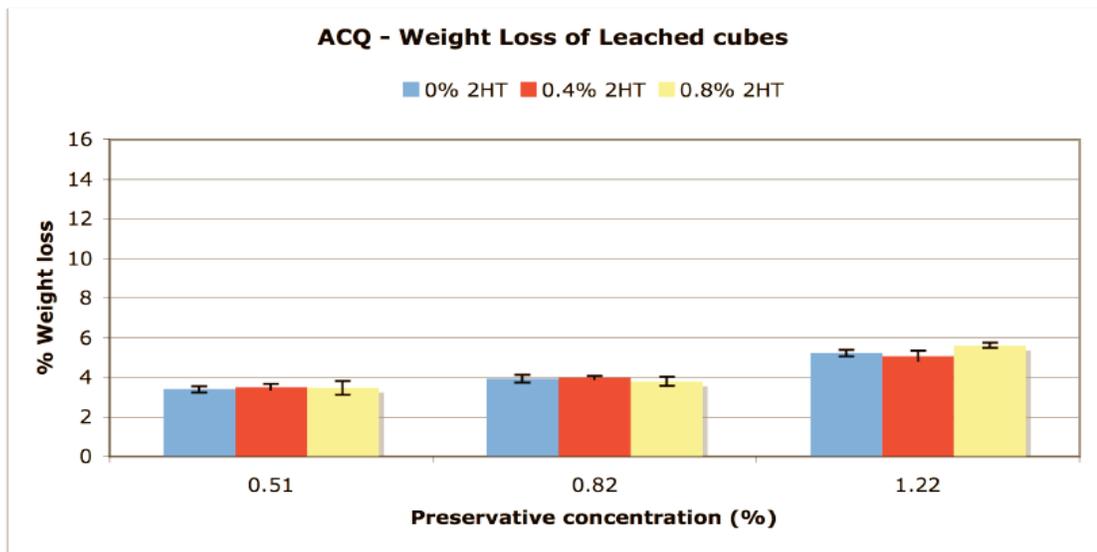


Figure 4.4. Effect of 2HT on resistance of leached ACQ treated southern pine sapwood blocks to attack by *Postia placenta* in a soil block test.

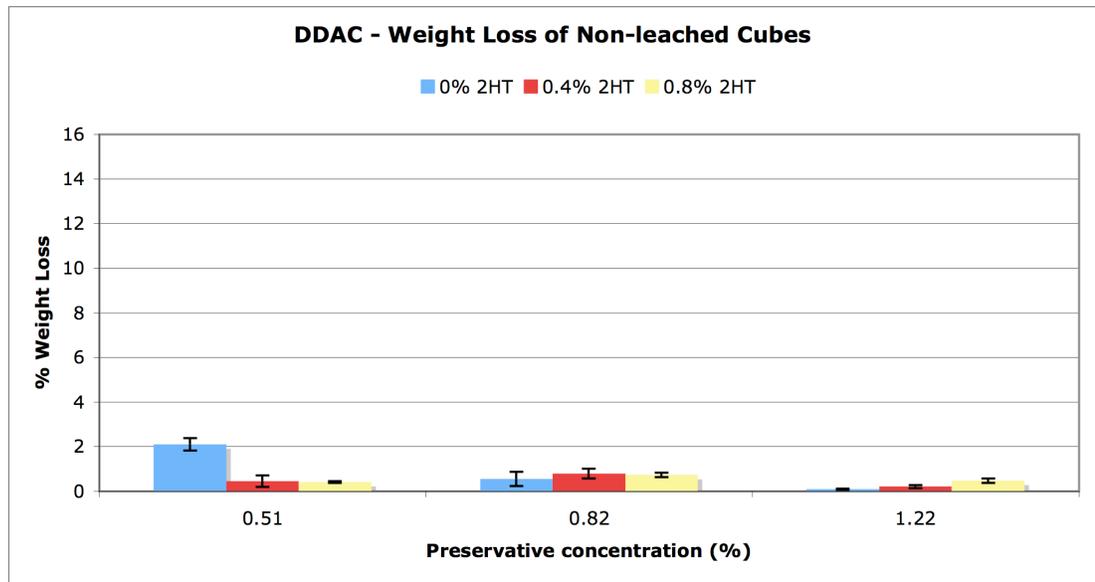


Figure 4.5. Effect of 2HT on resistance of non-leached DDAC treated southern pine sapwood blocks to attack by *Postia placenta* in a soil block test.

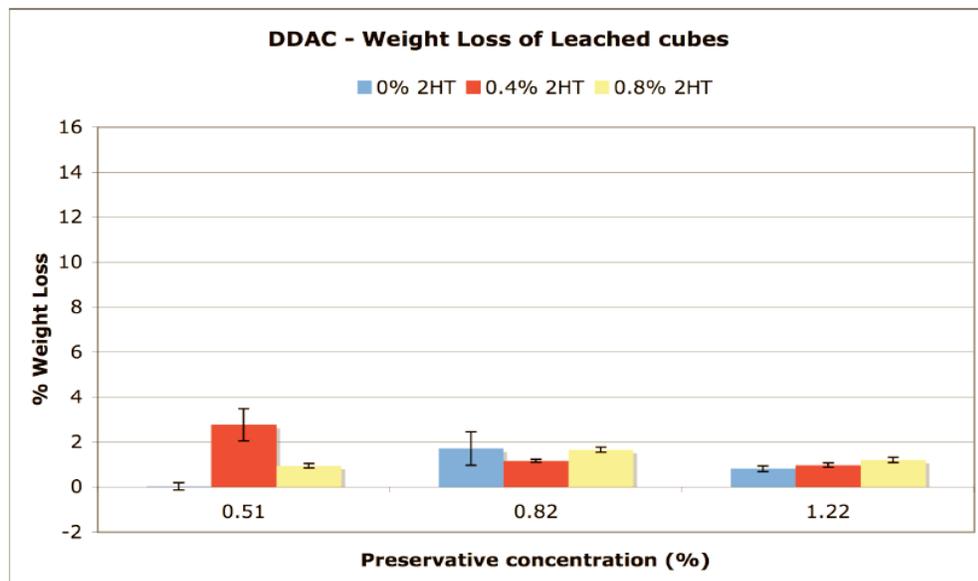


Figure 4.6. Effect of 2HT on resistance of leached DDAC treated southern pine sapwood blocks to attack by *Postia placenta* in a soil block test.

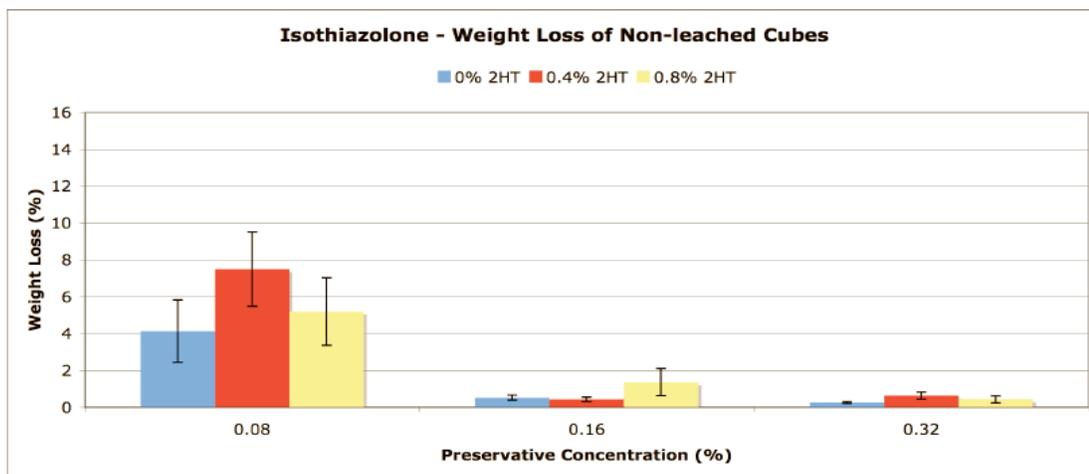


Figure 4.7. Effect of 2HT on resistance of non-leached isothiazolone treated southern pine sapwood blocks to attack by *Postia placenta* in a soil block test.

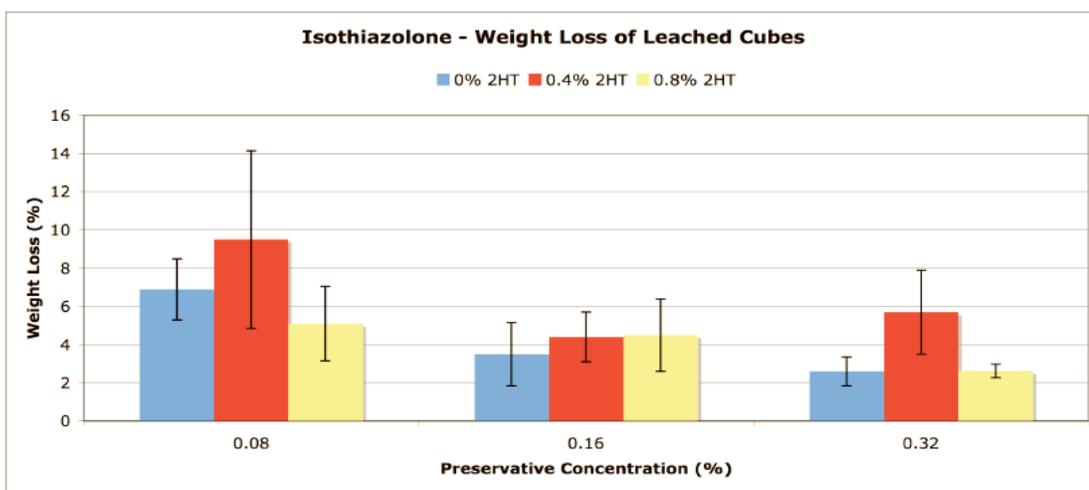


Figure 4.8. Effect of 2HT on resistance of leached isothiazolone treated southern pine sapwood blocks to attack by *Postia placenta* in a soil block test.

Preservative Type & 2HT (% a.l)	Target CuAz Level (kg/m ³)	Target Cu Level (kg/m ³)	Actual Cu Level (kg/m ³)
0.22% CuAz, 0% 2HT	1.7	1.6	2.0
0.22% CuAz, 0.4% 2HT	1.7	1.6	1.7
0.22% CuAz, 0.8% 2HT	1.7	1.6	1.7
0.42% CuAz, 0% 2HT	3.3	3.2	3.2
0.42% CuAz, 0.4% 2HT	3.3	3.2	3.1
0.42% CuAz, 0.8% 2HT	3.3	3.2	3.0
0.51% CuAz, 0% 2HT	4	3.8	3.4
0.51% CuAz, 0.4% 2HT	4	3.8	3.4
0.51% CuAz, 0.8% 2HT	4	3.8	3.5
0.82% CuAz, 0% 2HT	6.4	6.2	6.4
0.82% CuAz, 0.4% 2HT	6.4	6.2	6.6
0.82% CuAz, 0.8% 2HT	6.4	6.2	5.7
1.22% CuAz, 0% 2HT	9.6	9.2	8.5
1.22% CuAz, 0.4% 2HT	9.6	9.2	8.2
1.22% CuAz, 0.8% 2HT	9.6	9.2	8.5

Preservative Type & 2HT (% a.l)	Target ACQ-D Level (kg/m ³)	Target CuO Level (kg/m ³)	Actual CuO Level (kg/m ³)
0.51% ACQ type D, 0% 2HT	4	2.7	3.0
0.51% ACQ type D, 0.4% 2HT	4	2.7	3.1
0.51% ACQ type D, 0.8% 2HT	4	2.7	2.8
0.82% ACQ type D, 0% 2HT	6.4	4.3	4.8
0.82% ACQ type D, 0.4% 2HT	6.4	4.3	4.6
0.82% ACQ type D, 0.8% 2HT	6.4	4.3	3.1
1.22% ACQ type D, 0% 2HT	9.6	6.4	6.8
1.22% ACQ type D, 0.4% 2HT	9.6	6.4	6.7
1.22% ACQ type D, 0.8% 2HT	9.6	6.4	6.9

Table 4.2. Target and actual retentions of CuAz and ACQ in southern pine sapwood blocks treated with CuAz and ACQ with and without 2HT using vacuum/pressure processes.

Preservative Type & 2HT (% a.l)	Target DDAC Level (kg/m ³)	Actual Quat Level (kg/m ³)
0.51% DDAC, 0% 2HT	4	6.9
0.51% DDAC, 0.4% 2HT	4	7.9
0.51% DDAC, 0.8% 2HT	4	10.1
0.82% DDAC, 0% 2HT	6.4	10.3
0.82% DDAC, 0.4% 2HT	6.4	12.8
0.82% DDAC, 0.8% 2HT	6.4	13.9
1.22% DDAC, 0% 2HT	9.6	12.2
1.22% DDAC, 0.4% 2HT	9.6	16.9
1.22% DDAC, 0.8% 2HT	9.6	17.6

Preservative Type & 2HT (% a.l)	Target Isothiazolone Level (ppm)	Actual Isothiazolone Level (ppm)
0.08% RH287, 0% 2HT	800	927
0.08% RH287, 0.4% 2HT	800	409
0.08% RH287, 0.8% 2HT	800	521
0.16% RH287, 0% 2HT	1600	1651
0.16% RH287, 0.4% 2HT	1600	1097
0.16% RH287, 0.8% 2HT	1600	961
0.32% RH287, 0% 2HT	3200	3254
0.32% RH287, 0.4% 2HT	3200	1344
0.32% RH287, 0.8% 2HT	3200	1654

Table 4.3. Target and actual retentions of DDAC and ITH in southern pine sapwood blocks treated with DDAC and ITH with and without 2HT using a vacuum/pressure process.

CuAz Concentration (%)	Non- Leached			Leached		
	2HT Concentration (%)			2HT Concentration (%)		
	0	0.4	0.8	0	0.4	0.8
0.22	0.40 (0.09)	0.48 (0.11)	0.52 (0.05)	3.07 (0.84)	2.88 (0.09)	2.63 (0.06)
0.42	0.90 (0.11)	0.71 (0.18)	0.69 (0.18)	4.16 (0.28)	4.08 (0.25)	3.85 (0.20)
0.51	1.01 (0.10)	1.74 (0.24)	1.08 (0.20)	10.41 (3.04)	4.45 (0.13)	4.07 (0.59)
0.82	0.67 (0.19)	0.51 (0.12)	0.34 (0.17)	5.23 (0.51)	5.41 (0.13)	5.23 (0.16)
1.22	0.50 (0.24)	1.35 (0.23)	0.75 (0.21)	6.38 (0.34)	6.59 (0.19)	6.98 (0.18)

Values represent means of 6 replicates per treatment while figures in parenthesis represent one standard deviation.

Table 4.4. Effect of 2HT on the ability of copper azole (CuAz) to protect leached and non-leached southern pine sapwood against attack by *Postia placenta* in a soil block.

Coefficients:	Estimate	Std. Error	t value	p value
Intercept	2.1285	0.3059	6.9586	< 0.001
Concentration	1.6525	0.321	4.5639	0.000008
Treatment	-2.1298	0.1268	-16.7929	< 0.001
2HT	-0.6936	0.3872	-1.7911	0.075

Residual standard error: 1.697 on 175 degrees of freedom

Multiple R-Squared: 0.6364

F-statistic: 102.1 on 3 and 175 DF, p-value: 0

Table 4.5. Summary multiple linear regression results of weight loss data from southern pine sapwood blocks treated with CuAz with or without 2HT then leached or left non-leached prior to exposure to *P. placenta* in a soil block test. The variable “Treatment” stands for leached or non-leached blocks.

	D.F.	Sum Sq	Mean Sq	F value	p value
Concentration	1	60.8782	60.8782	21.145	0.000008
2HT	1	811.9053	811.9053	282.002	0.075006
Treatment	1	9.2362	9.2362	3.208	< 0.001
Residuals	175	503.8384	2.8791		

Table 4.6. ANOVA table for weight loss data from southern pine sapwood blocks treated with CuAz with or without 2HT then leached or left non-leached prior to exposure to *P. placenta* in a soil block test.

ACQ-D Concentration (%)	Non-Leached			Leached		
	2HT Concentration (%)			2HT Concentration (%)		
	0	0.4	0.8	0	0.4	0.8
0.51	-0.31 (0.20)	0.92 (0.15)	0.54 (0.17)	3.39 (0.15)	3.49 (0.17)	3.47 (0.35)
0.82	0.29 (0.10)	-0.02 (0.19)	0.62 (0.17)	3.93 (0.19)	3.97 (0.11)	3.79 (0.23)
1.22	0.79 (0.36)	-0.12 (0.13)	0.32 (0.22)	5.22 (0.16)	5.06 (0.27)	5.61 (0.13)

Values represent means of 6 replicates per treatment while figures in parenthesis represent one standard deviation.

Table 4.7. Effect of 2HT on the ability of ACQ to protect leached and non-leached southern pine sapwood against attack by *Postia placenta* in a soil block.

Coefficients:	Estimate	Std. Error	t value	p value
Intercept	5.1664	0.2166	23.848	2.00E-16
Concentration	-1.2219	0.2147	-5.691	1.17E-07
Treatment	-3.8768	0.1248	-31.065	2.00E-16
2HT	0.2152	0.1911	1.126	0.263

Residual standard error: 0.6485 on 104 degrees of freedom

Multiple R-Squared: 0.9057, Adjusted R-squared: 0.903

F-statistic: 332.9 on 3 and 104 DF, p-value: < 2.2e-16

Table 4.8. Summary multiple linear regression results of weight loss data from southern pine sapwood blocks treated with ACQ with or without 2HT then leached or left non-leached prior to exposure to *P. placenta* in a soil block test. The variable "Treatment" stands for leached or non-leached blocks.

	D.F.	Sum Sq	Mean Sq	F value	p value
Concentration	1	13.62	13.62	32.3888	1.17E-07
2HT	1	0.53	0.53	1.2686	0.263
Treatment	1	405.81	405.81	965.0079	2.00E-16
Residuals	104	43.73	0.42		

Table 4.9. ANOVA table for weight loss data from southern pine sapwood blocks treated with ACQ with or without 2HT then leached or left non-leached prior to exposure to *P. placenta* in a soil block test.

DDAC Concentration (%)	Non-Leached			Leached		
	2HT Concentration (%)			2HT Concentration (%)		
	0	0.4	0.8	0	0.4	0.8
0.51	0.59 (0.28)	0.45 (0.26)	0.41 (0.04)	0.04 (0.16)	2.77 (0.71)	0.95 (0.09)
0.82	0.56 (0.32)	0.80 (0.22)	0.74 (0.10)	1.72 (0.74)	1.17 (0.07)	1.66 (0.11)
1.22	0.10 (0.03)	0.21 (0.07)	0.48 (0.10)	0.82 (0.13)	0.98 (0.09)	1.21 (0.12)

Values represent means of 6 replicates per treatment while figures in parenthesis represent one standard deviation.

Table 4.10. Effect of 2HT on the ability of DDAC to protect leached and non-leached southern pine sapwood against attack by *Postia placenta* in a soil block.

	Estimate	Std. Error	t value	p value
Coefficients:				
Intercept	1.4564	0.247	5.897	4.65E-08
Concentration	-0.4082	0.2448	-1.668	0.0984
Treatment	0.3732	0.2178	1.714	0.0896
2HT	-0.7929	0.1423	-5.573	1.98E-07

Residual standard error: 0.7393 on 104 degrees of freedom

Multiple R-Squared: 0.2612, Adjusted R-squared: 0.2399

F-statistic: 12.26 on 3 and 104 DF, p-value: 6.244e-07

Table 4.11. Summary multiple linear regression results of weight loss data from southern pine sapwood blocks treated with DDAC with or without 2HT then leached or left non-leached prior to exposure to *P. placenta* in a soil block test. The variable "Treatment" stands for leached or non-leached blocks.

	D.F.	Sum Sq	Mean Sq	F value	p value
Concentration	1	1.52	1.52	2.7816	0.09836
2HT	1	1.605	1.605	2.9361	0.0896
Treatment	1	16.976	16.976	31.0583	1.98E-07
Residuals	104	56.844	31.0583		

Table 4.12. ANOVA table for weight loss data from southern pine sapwood blocks treated with DDAC with or without 2HT then leached or left non-leached prior to exposure to *P. placenta* in a soil block test.

Isothiazolone Concentration (%)	Non-Leached			Leached		
	2HT Concentration (%)			2HT Concentration (%)		
	0	0.4	0.8	0	0.4	0.8
0.08	4.1 (1.7)	7.4 (2.0)	5.2 (1.8)	6.9 (1.6)	9.5 (4.6)	5.1 (1.9)
0.16	0.52 (0.1)	0.4 (0.1)	1.4 (0.7)	3.5 (1.7)	4.4 (1.3)	4.5 (1.9)
0.32	0.2 (0.1)	0.6 (0.19)	0.4 (0.2)	2.6 (0.8)	5.7 (2.2)	2.62 (0.4)

Values represent means of 6 replicates per treatment while figures in parenthesis represent one standard deviation.

Table 4.13. Effect of 2HT on the ability of isothiazolone to protect leached and non-leached southern pine sapwood against attack by *Postia placenta* in a soil block.

Coefficients:	Estimate	Std. Error	t value	p value
Intercept	1.3472	0.1853	7.2685	< 0.001
Concentration	-2.8643	0.7571	-3.7831	0.0002858
Treatment	0.2789	0.2266	1.2308	0.0000054
2HT	-0.3646	0.0756	-4.8228	0.2443748

Residual standard error: 0.7521 on 95 degrees of freedom
 Multiple R-Squared: 0.2901, Adjusted R-squared: 0.04969
 F-statistic: 12.94 on 3 and 95 DF, p-value: 3.691e-07

Table 4.14. Summary multiple linear regression results of weight loss data from southern pine sapwood blocks treated with isothiazolone with or without 2HT then leached or left non-leached prior to exposure to *P. placenta* in a soil block test. The variable "Treatment" stands for leached or non-leached blocks.

	D.F.	Sum Sq	Mean Sq	F value	p value
Concentration	1	8.02901	8.02901	14.19531	0.0002858
2HT	1	0.77609	0.77609	1.37214	0.2443748
Treatment	1	13.15584	13.15584	23.25956	0.0000054
Residuals	95	53.73296	0.56561		

Table 4.15. ANOVA table for weight loss data from southern pine sapwood blocks treated with isothiazolone with or without 2HT then leached or left non-leached prior to exposure to *P. placenta* in a soil block test.

**CHAPTER 5 – INTERACTIONS BETWEEN WOOD COMPONENTS AND
2HT IN ACQ, COPPER AZOLE, DDAC, AND ISOTHIAZOLONE
FORMULATIONS BY FTIR SPECTROSCOPY**

June Mitsuhashi

Jeffrey J. Morrell

Abstract

The incorporation of additives into preservative formulations could help limit leaching of preservative components from treated wood in or near aquatic environments. Di(hydrogenated tallowalkyl)dimethyl ammonium chloride (2HT), a common fabric softener, has been shown to affect copper and DDAC mobility in treated wood by improving the water repellency of the treated member. Fourier Transform Infrared Spectroscopy (FTIR) was used to study interactions between cellulose, vanillin, xylan, or lignin and ACQ, CuAz, DDAC or isothiazolone with and without 2HT. The addition of 2HT to solutions of ACQ, CuAz, and DDAC failed to produce changes in structure for any of the wood components studied. The results suggest that the cationic end of 2HT interacts with the negative surface charge of wood, exposing the hydrophobic end of 2HT to create a water repellent surface. The result is a surface that resists moisture, and thereby limits leaching of preservative components.

Introduction

The withdrawal of chromated copper arsenate (CCA) from residential applications has led the industry to shift to alternative preservatives such as alkyl copper quat (ACQ) and copper azole (CuAz). These preservative

systems have the disadvantage of lacking a strong agent for fixing copper to the wood and contain much higher levels of copper than CCA. For this reason, copper from wood treated with ACQ or CuAz tends to migrate more easily than from CCA treated wood.

Wood consists of three main polymeric materials: cellulose microfibrils, hemicelluloses, and lignin along with small amounts of extractives. These components play an important role in the absorption and fixation of copper-based preservatives. CCA reacts mainly with lignin as copper chromate or copper arsenate or physically precipitates onto cellulose as organic salts. CCA components can also form complexes between metal ions and polyflavanoid tannin extractives (Dahlgren, 1975; Pizzi, 1982). Amino-copper preservative systems tend to be deposited in wood through chemical reactions of the preservative component with carboxylic acid groups in hemicellulose and especially with phenolic hydroxyl groups in lignin (Humar and Petrie, 2000; Zhang and Kamdem, 2000a). Fixation is directly correlated with the number of anionic sites in wood. Amines and copper compete for the same limited number of reaction sites in wood (Jiang and Ruddick, 1999, 2004; Tascioglu et. al., 2005).

Reactions between preservatives and the wood that result in “fixation” are increasingly important because of concerns over heavy metal migration

from the wood into surrounding environments. While some metal must be available in liquid within the wood cell for the preservative to function, excess metal migration can have significant effects on non-target organisms, especially in aquatic environments. While treatment regimes can be altered to reduce the risk of over-treatment that increases subsequent preservative migration, developing methods for better fixation of preservative components could also markedly reduce the risk of leaching.

The use of additives in treatment solutions to protect wood from weathering or leaching of preservative component represents one approach for reducing the risk of preservative migration following treatment. Preliminary research suggests that Di(hydrogenated tallowalkyl)dimethyl ammonium chloride (Arquad 2HT-75, Akzo Nobel Inc.) (2HT), a commonly used fabric softener, decreased the leaching rate of copper from treated wood exposed in or near aquatic environments (Jin et. al., 2006). 2HT is a cationic surfactant based on a hydrogenated tallow amine ($R_2 - N^+(CH_3)_2 Cl$). The alkyl chain distribution of 2HT consists of mostly long carbon chains (64% C_{18} and 31% C_{16}). 2HT contains a positively charged cationic end that is hydrophilic due to the net positive charge of the amine group and a negative anionic end that is hydrophobic due to the long hydrocarbon radical (Davidson et. al., 1960). Biocidal activity of quaternary ammonium compounds depends on the length of alkyl chains. Short alkyl chains, like those found in DDAC, provide

protection against fungi and insect attack. The long alkyl chains on 2HT limit its biocidal activity (Jin et. al., 2006).

A 10 day leaching test of southern yellow pine boards (89x39x305 mm) treated to different retentions with alkyl copper quat Type D (ACQ-D) with and without 2HT showed that the presence of 2HT produced a 75 % reduction in copper loss. Soil-bed decay tests on ACQ treated stakes with and without 2HT resulted in a 33-50% reduction in copper loss from 2HT treated stakes after 10 years of exposure (Jin et. al, 2006). These trials suggested that small amounts of 2HT limited copper migration from treated wood, but the mechanism by which copper movement was affected was unknown.

Crutzen (1995) suggested that hydrophobic interactions enable 2HT sorption on cellulose. During dilution, fatty acid chains on the 2HT in contact with water are hydrophobically expelled out of the aqueous phase and deposited onto cellulose through a combination of van der Waals interactions and, to a lesser degree, electrostatic attractions (in the case of negatively charged surfaces). Although 2HT is strongly charged, this charge serves only as a dispersing agent and not as an anchorage (Crutzen, 1995). As a result, 2HT also deposits on charge-free cellulose. Increasing the cellulose surface area in contact with 2HT increases the rate and overall amount of deposition. The organic cationic end balances the negative surface charge in the

presence of negatively charged substrates, exposing the hydrophobic end and creating water repellent surfaces (Davidson et. al., 1960). Electrostatic repulsion between absorbed ions by hydrophobic interactions eventually limits 2HT sorption onto cellulose. The limited cellulose sorption results in a monolayer of 2HT, although negatively charged substrates can form a double layer, thus enhancing water repellency (Ramsbotham, 1989). Ionic interaction forces, based on an electrostatic model, have also been proposed as the driving force in sorption of 2HT on textile surfaces. The affinities between long hydrophobic chains are “above and beyond” that possible from electrostatic interactions (White, 1970), suggesting that other factors contribute 2HT sorption on cellulosic materials.

The potential mechanisms by which 2HT alters copper losses from wood remain unclear. While improved water repellency could slow wetting and drying cycles, thereby reducing the overall chemical losses, other water repellants have not produced the reductions in copper losses noted with this compound. These results suggest that 2HT may have other, more subtle effects on copper mobility.

The potential for interactions between 2HT and various wood components was investigated by exposing treatment solutions to native or extractive free, ground southern pine sapwood as well as various wood

components and then examining the resulting treatment solutions for evidence of reactions using Fourier transform infrared spectroscopy (FTIR). FTIR is a valuable tool that allows the identification of the structure of organic molecules (Nakanishi and Solomon, 1977).

Materials and Methods

Extractive free wood was produced by grinding southern pine sapwood to pass a 100 mesh screen, then subjecting this material to hot water extraction according to ASTM Standard D1110-84 (ASTM, 2005) for water solubility. Organosolv lignin and cellulose were obtained from Aldrich Chemical Co. (Milwaukee, WI), vanillin was obtained from JT Baker (Phillipsburg, NJ), and xylan was obtained from Sigma Chemicals (St. Louis, MO).

One gram of a given wood component was treated with 20 g of the respective treating solution (Table 5.1). The solutions were continuously stirred while being heated to 35°C for 24 hours. The heat was needed to prevent the 2HT from flocculating from the solution. At the end of the exposure period, the sawdust was filtered and washed with a minimum of deionized water to remove any non-reacted preservative components. Sawdust treated with copper as either ACQ or CA were stored wet for 72

hours at 20-23 C, and then washed. The resulting sawdust samples were oven-dried (50°C) and retained for later analysis.

Preservative	Preservative Concentration (%)		
	2HT Concentration (%)		
	0	0.4	0.8
ACQ-D (%)	1.22	-	1.22
DDAC (%)	1.22	-	1.22
Copper Azole-B (%)	0.51	-	0.51
Isothiazolone (%)	0.32	-	0.32
2HT (%)	-	0.4	0.8

Table 5.1. Treatment combinations used to assess the ability of 2HT to react with wood components (percent by mass).

The dry sawdust was mixed with potassium bromide and the resulting mixture was compressed into a pellet that was assessed using a Nexus 470 FTIR Spectrophotometer (Minneapolis, MN). Spectra were collected from 50 scans per sample at a resolution of 16 cm⁻¹ over a range of 800-4000 cm⁻¹. The resulting spectra were assessed for changes in peak ratios related to lignin, cellulose or xylan that could be suggestive of interactions between a respective component and the preservative system. Particular attention was given to changes in spectra that occurred when 2HT was present in the wood components that were treated with the different preservative systems.

Results and Discussion

Since 2HT could not be oven dried into a solid state, the band between 3570 cm^{-1} and 3200 cm^{-1} is attributed to the O-H stretching of water in the sample (Figure 5.1)(Coates, 2000). The quaternary amine was not obvious in the spectra because it lacks a characteristic band in FTIR spectroscopy (Nakanishi and Solomon, 1977). The narrow bands at 2918 cm^{-1} and 2844 cm^{-1} represent the stretching of CH_2 groups (Coates, 2000). These peaks were later shown to be the only group that interacted with the different wood components. Peaks from the DDAC spectra (Zhao et. al., 2004), another quaternary ammonium compound, coincided with those found in the spectra of 2HT, suggesting that 2HT and DDAC have similar interactions with wood components. Research suggests that quaternary ammonium compounds do not react with the wood, but only couple with wood through an ion exchange process with phenolic hydroxyls in lignin and xylan (Preston et. al., 1987; Tascioglu et. al., 2005).

No differences were observed in the spectra from untreated or 2HT treated cellulose, lignin and vanillin (Figure 5.2 and 5.3A). Spectra from vanillin and xylan treated with 2HT contained bands at $2970\text{-}2950/2880\text{-}2860\text{ cm}^{-1}$ (Figure 5.3A) and $2935\text{-}2915/2865\text{-}2845\text{ cm}^{-1}$ (Figure 5.3B) (Coates,

2000) that are attributed to C-H stretching of methylene ($>CH_2$) groups. These bands were intensified by incorporation of 2HT, suggesting that methylene groups were being held by vanillin and xylan through ion exchange.

Comparisons between untreated and ACQ treated cellulose (Figure 5.4A) showed the appearance of a band at 1600 cm^{-1} with ACQ. This band was attributed to N-H bending of the amine and agrees with previous research showing little evidence of hydrogen bonding between hydroxyl groups in cellulose and nitrogen from the amine that would produce copper-amine-cellulose complexes (Cooper, 1991; Jin and Preston, 1991; Kamdem and Zhang, 2000; Rennie et. al., 1987).

There was no evidence of spectral changes between the untreated, ACQ treated and ACQ+2HT treated xylan (Figure 5.4B), although there was some intensification of previously mentioned CH groups, 2913 cm^{-1} and 2848 cm^{-1} , due to the incorporation of quaternary ammonium compounds. The strengthening of these bands was also observed in lignin (Figure 5.5), along with a reduction of the intensity of the peak 1706 cm^{-1} between untreated and ACQ treated lignin. This band represents conjugated esters that link various benzoic acid types found in lignin that are susceptible to alkaline hydrolysis (Sarkanen et. al., 1967). These results validate previous studies suggesting

that ester groups in lignin are the reactive sites for copper amine fixation reactions (Humar and Petrie, 2000; Thomason and Pasek, 1997; Zhang and Kamdem, 2000a).

Comparisons between spectra of untreated and ACQ treated vanillin, a model compound with some of the same reactive sites in lignin (Figure 5.6A), revealed that the treatment altered peak heights in the range 1700-1000 cm^{-1} . Intensity peaks at 1668 cm^{-1} , 1590 cm^{-1} , 1513 cm^{-1} , 1416 cm^{-1} , 1422 cm^{-1} , 1306 cm^{-1} , 1267 cm^{-1} , 1209 cm^{-1} , 1196 cm^{-1} , 1022 cm^{-1} , 873 cm^{-1} , 815 cm^{-1} , and 725 cm^{-1} appeared to be lowered by the treatment. A reduction in the intensity of the carbonyl stretching of the aldehyde group, 1668 cm^{-1} , was evident after ACQ treatment. The disappearance of peaks 1209 and 1196 assigned to phenolic hydroxyl groups (Nakanishi and Solomon, 1977; Sarkanen et. al., 1967) support evidence that the quaternary ammonium compound reacts with phenolic hydroxyls in lignin (Jin and Preston, 1991). The decreased intensity of peaks at 1590 cm^{-1} , 1513 cm^{-1} , and 1422 cm^{-1} , which are attributed to aromatic skeletal vibrations; especially the lessening of band 1422 cm^{-1} which is highly sensitive to the nature of ring substituents, further suggests that the substituents have been changed. These results provide further evidence that the ethanolamine, an ACQ component, reacts with substituted benzene ring groups in lignin (Humar and Petrie, 2000; Thomason and Pasek, 1996; Zhang and Kamdem, 1999). The broad peak in

the 3600~2500 region, assigned to oxygen-hydrogen stretching (Nakanishi and Solomon, 1977) was significantly altered, revealing a distinct peak, 2919 cm^{-1} , associated with the saturated aliphatic groups of the quaternary ammonium compound (Coates, 2000; Zhao, et. al. 2004).

Treatment of vanillin with 2HT amended ACQ (Figure 5.6B) reduced the bands 1211 cm^{-1} and 1050 cm^{-1} , attributed to primary alcohol and phenolic hydroxyl groups, suggesting that 2HT had the same potential reaction sites as DDAC (Jin and Preston, 1991; Coates, 2000). Stretching of CH bound groups was observed at 2927 cm^{-1} and 2848 cm^{-1} , due to ionic interactions of hydroxyl groups with the quaternary ammonium compound.

A reduction in peak intensity at 1706 cm^{-1} , which can be attributed to esters linking to various types of benzoic acids in lignin (Sarkanen, et al, 1967), was also observed between untreated and CuAz treated lignin (Figure 5.7B). This effect was most likely due to the amines found in CuAz. There was no change in the spectra between treated and non-treated cellulose and xylan. As previously seen with other preservative treatments, the only difference observed between CuAz and CuAz +2HT treatments on lignin, vanillin, and xylan (Figures 5.7A, 5.8, and 5.9) was the elongation of methyl and methylene groups due to the continuous increase of ionic interaction forces bounding quaternary ammonium compounds (DDAC and 2HT).

FTIR spectra of cellulose, lignin, and vanillin did not differ after being treated with DDAC or DDAC+2HT (Figures 5.10 and 5.11). The only differences observed between treated and untreated xylan was the elongation of the band 2926 cm^{-1} and 2848 , attributed to methyl and methylene groups of the quaternary ammonium compound.

No changes in the spectra of cellulose and lignin were observed following the incorporation of isothiazolone and 2HT to the treatment (Figures 5.12 and 5.13). The only change in FTIR spectra observed with 2HT in vanillin was the elongation of the 2919 cm^{-1} band between vanillin and isothiazolone treated vanillin. This band disappeared once 2HT was incorporated to the treatment (Figure 5.13A) suggesting that any effect that isothiazolone might have in vanillin is negated by incorporating 2HT into the formulation. A peak in the lignin and xylan spectra, at 2350 cm^{-1} and 2345 cm^{-1} respectively, appeared with the incorporation of 2HT to the isothiazolone treatment. This peak was not attributed to lignin or xylan in the literature, but might be due to the anti-symmetric stretching of carbon dioxide (2349 cm^{-1}) (Nakanishi and Solomon, 1977). Various peaks appeared when xylan was treated with isothiazolone (Figure 5.13B). The formation of a 1725 cm^{-1} peak was associated with the stretching vibration of the carbonyl group contained in isothiazolone. Peaks at 1250 cm^{-1} and 1170 cm^{-1} are attributed to skeletal

stretching of methyl groups found in both isothiazolone and 2HT (Nakanishi and Solomon, 1977; Pretsch et. al., 2000). Peak 998 cm^{-1} is due to C-N stretching of isothiazolone, although the literature suggests that it has no practical significance (Prestch, et. al. 2000). Peak 705 cm^{-1} is attributed to the S-C skeletal vibration of isothiazolone (Pretsch et. al, 2000). All these peaks coincide with the peaks found in isothiazolone (Figure 5.14) indicating that 2HT did not affect the spectra of xylan.

Attempts to assess the effects of 2HT on ACQ and CuAz interactions with water-soluble extractives were unsuccessful due to the inability to recover sufficient quantities of extractives from the test material to produce detectable changes (Figure 5.15).

The lack of absorption of CuAz, DDAC, and isothiazolone onto cellulose was likely due to the poor reactivity of aliphatic hydroxyl groups in cellulose molecules. Cellulose contains large amounts of primary and secondary hydroxyl groups that form hydrogen bonds within and between cellulose chains. This crystalline system restrains cellulose reactivity because the hydrogen bond arrangement impedes bonding with other molecules (Kamdem and Zhang, 2000).

Conclusions

FTIR spectroscopic analysis suggests that 2HT in solutions of ACQ-D, CuAz, or DDAC does not appear to react with any of the wood components studied. Previous studies have suggested that ionic interactions between the organic cationic end of the quaternary compound and the negative surface charge of wood exposes the hydrophobic end of the 2HT, to create a water repellent surface. This surface reduces moisture uptake, thereby limiting leaching of preservative components. 2HT did not appear to have the same effect on wood components in the presence of isothiazolone; suggesting that incorporation of 2HT into isothiazolone formulations might have negative effects on the performance of this preservative.

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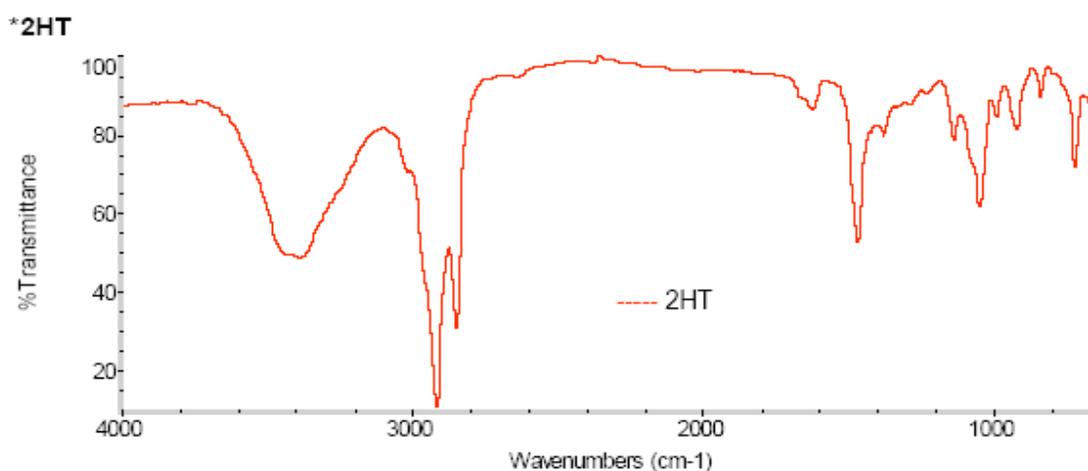


Figure 5.1. FTIR Spectra of 2HT.

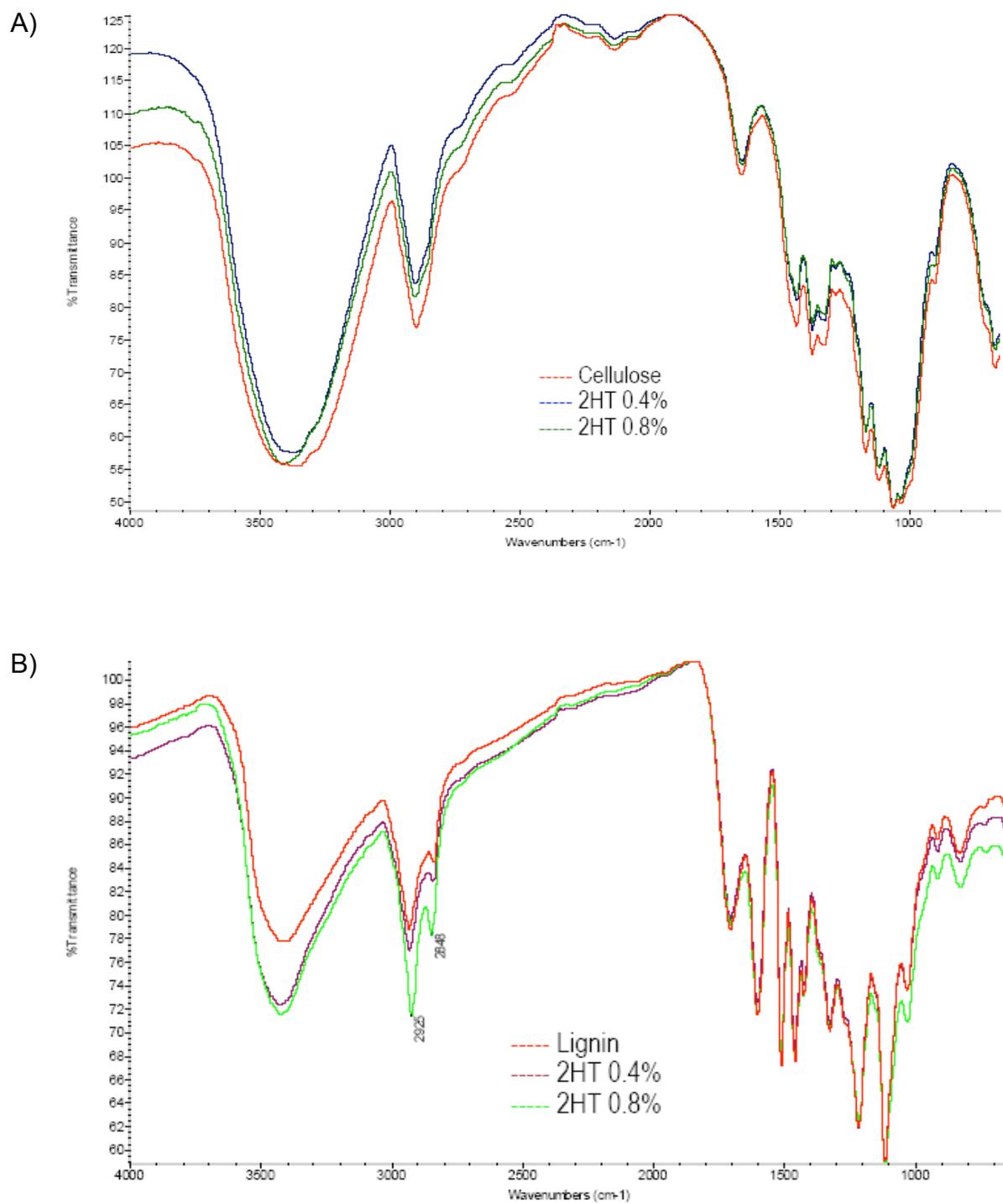


Figure 5.2. Comparison between FTIR spectra of untreated and 2HT treated A) cellulose and B) lignin.

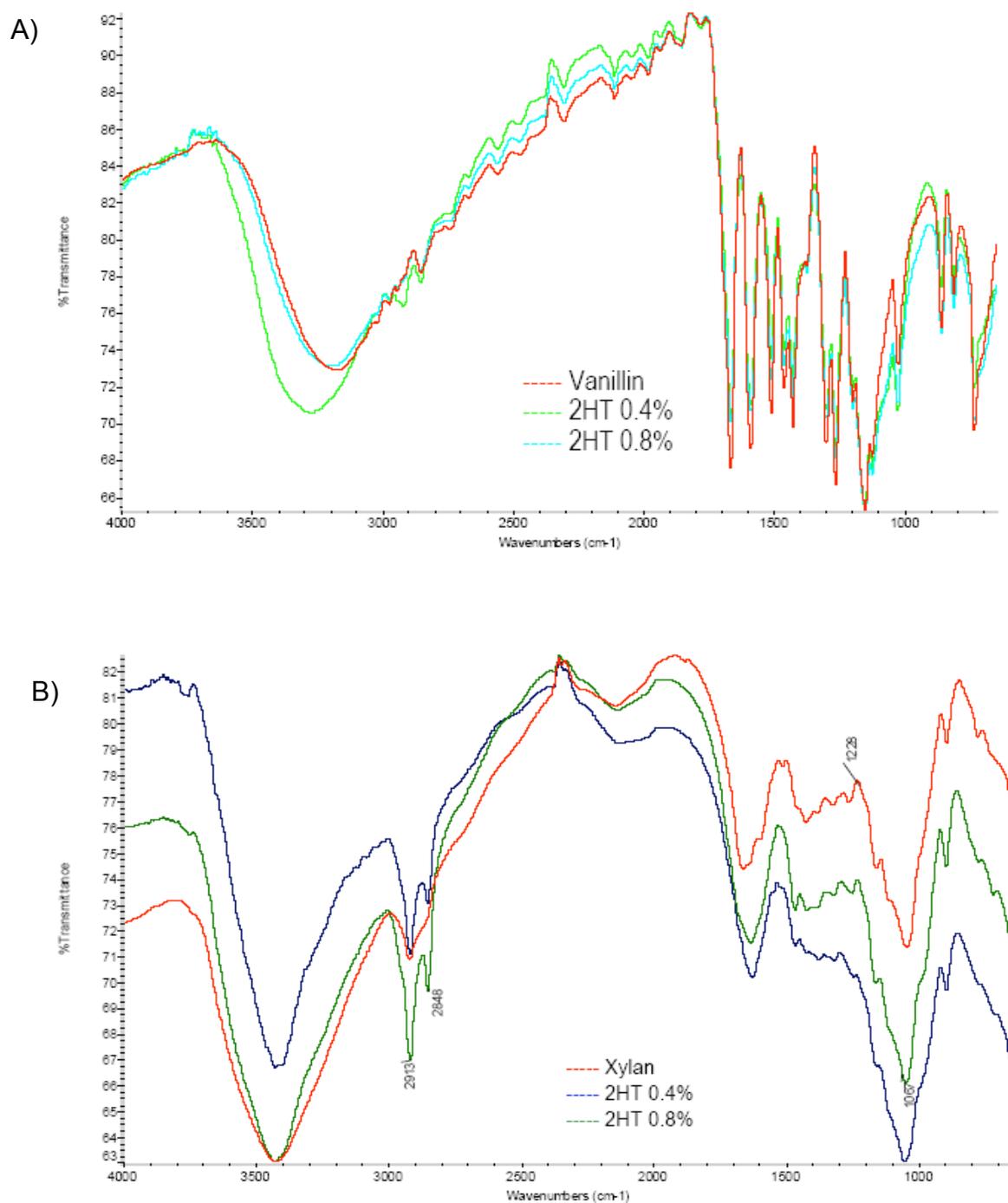


Figure 5.3. Comparison between FTIR spectra of untreated and 2HT treated A) vanillin and B) xylan.

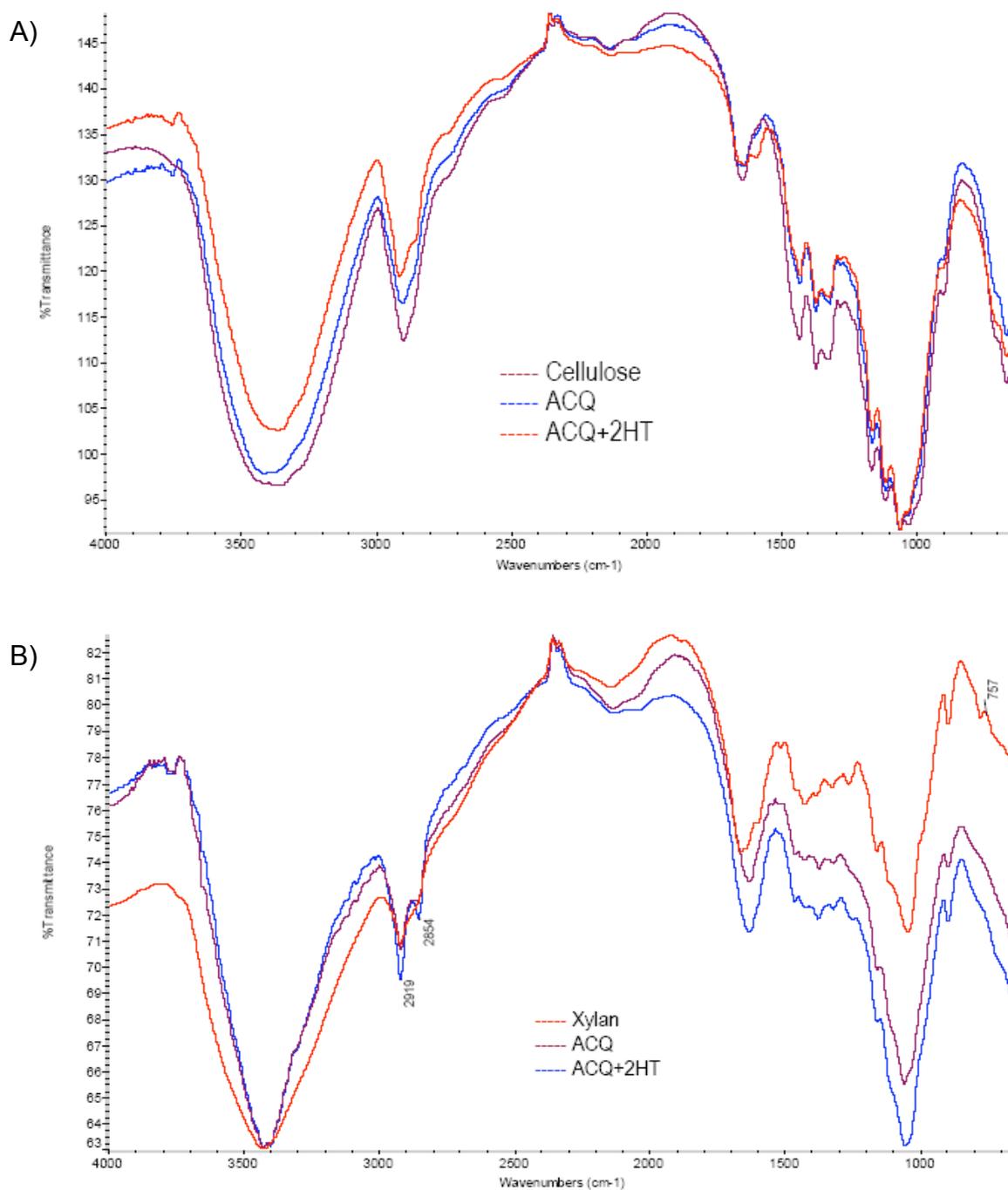


Figure 5.4. Comparison between FTIR spectra of untreated, ACQ and ACQ+2HT treated A) cellulose and B) xylan.

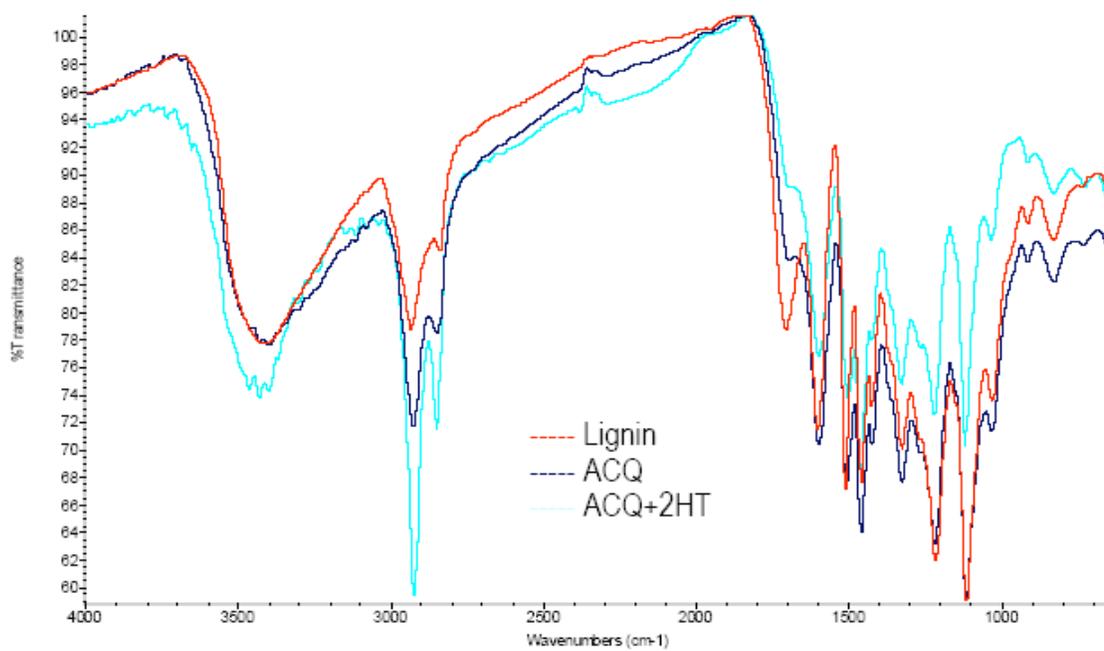


Figure 5.5. Comparisons between FTIR spectra of untreated, ACQ and ACQ+2HT treated lignin.

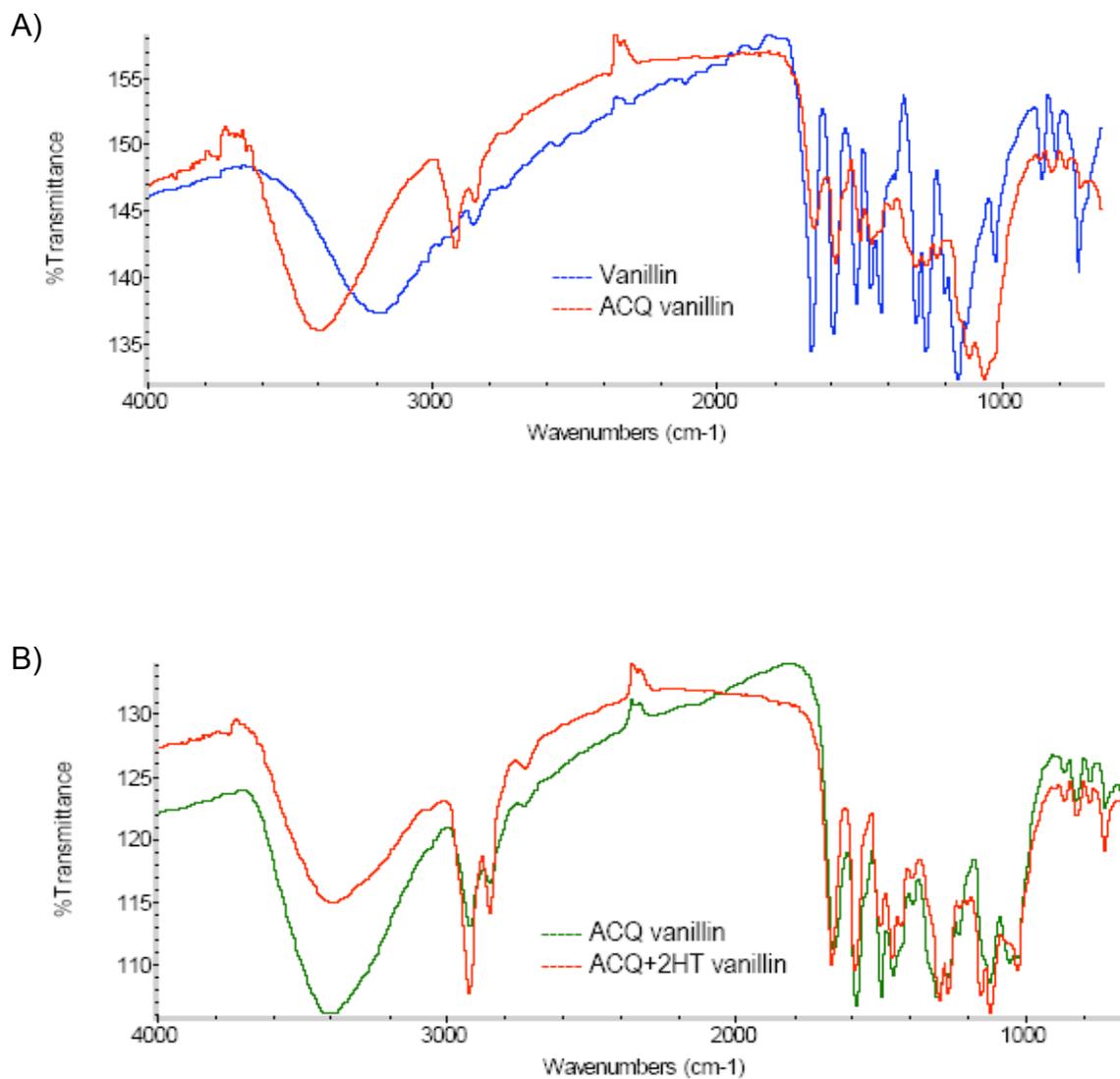


Figure 5.6. Comparisons between FTIR spectra of A) untreated and ACQ treated vanillin and B) ACQ and ACQ+2HT treated vanillin.

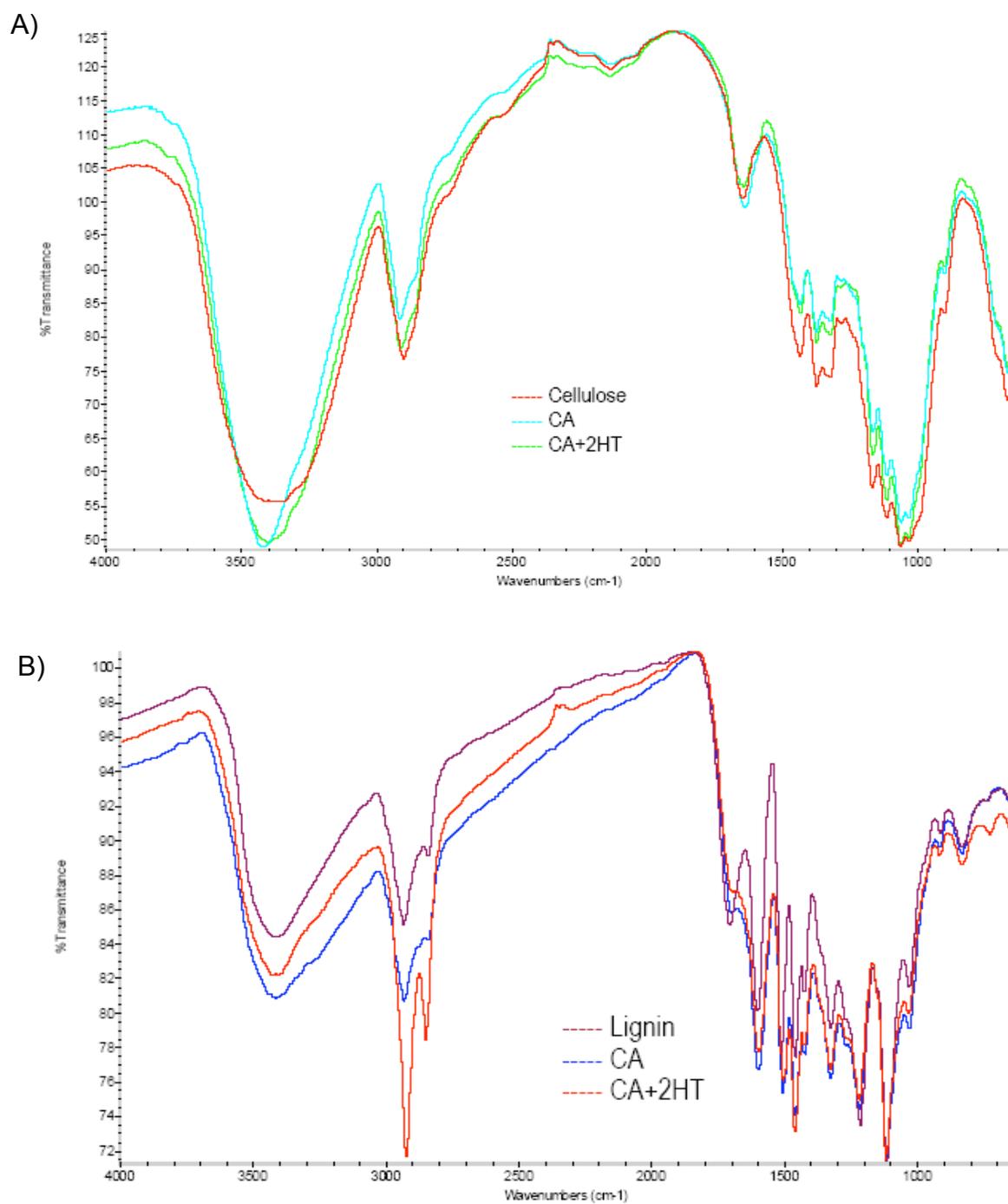


Figure 5.7. Comparisons between FTIR spectra for untreated, CuAz, and CuAz +2HT treated A) cellulose and B) lignin.

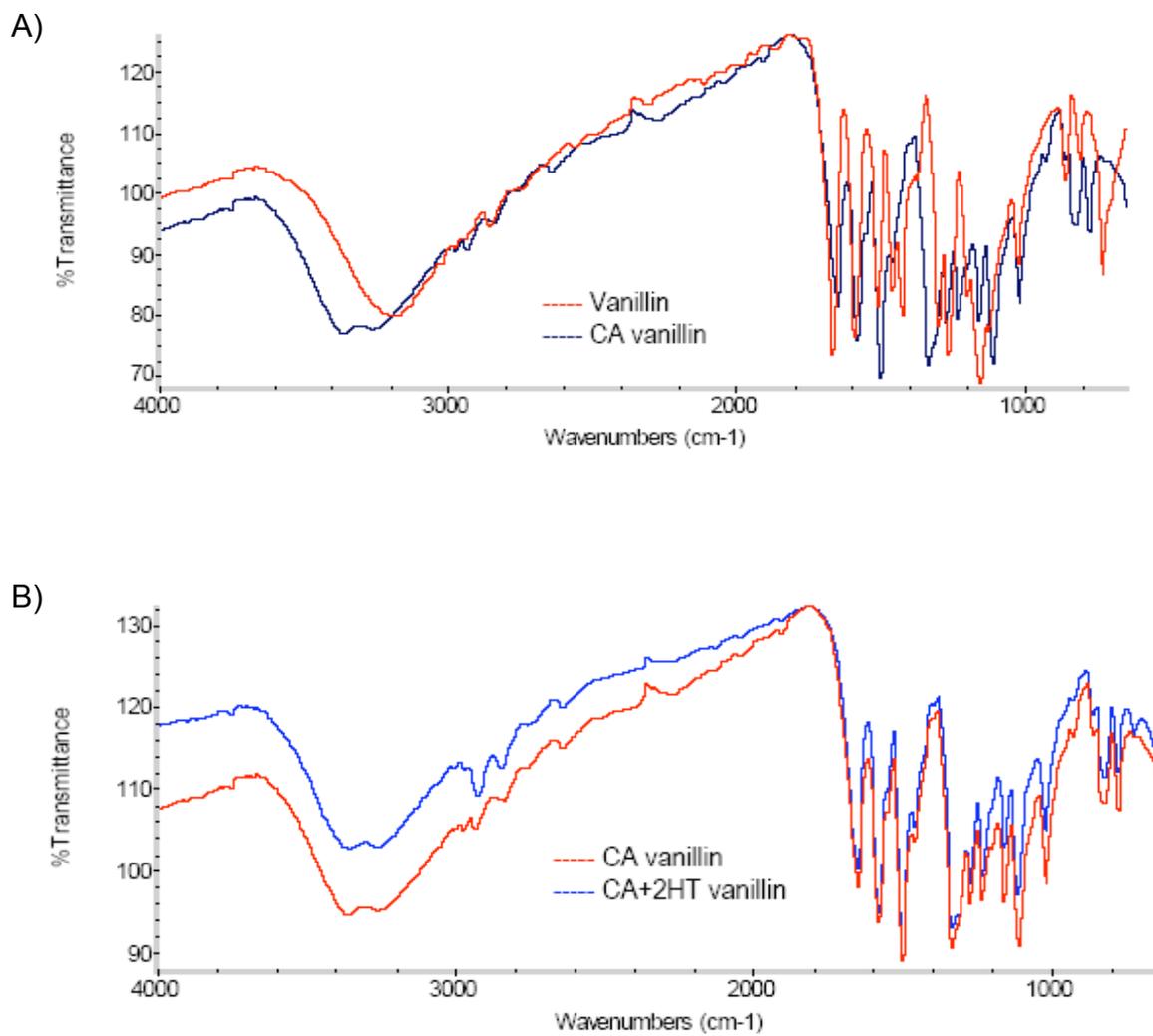


Figure 5.8. Comparisons between FTIR spectra for A) untreated and CuAz treated vanillin and B) CuAz and CuAz +2HT treated vanillin.

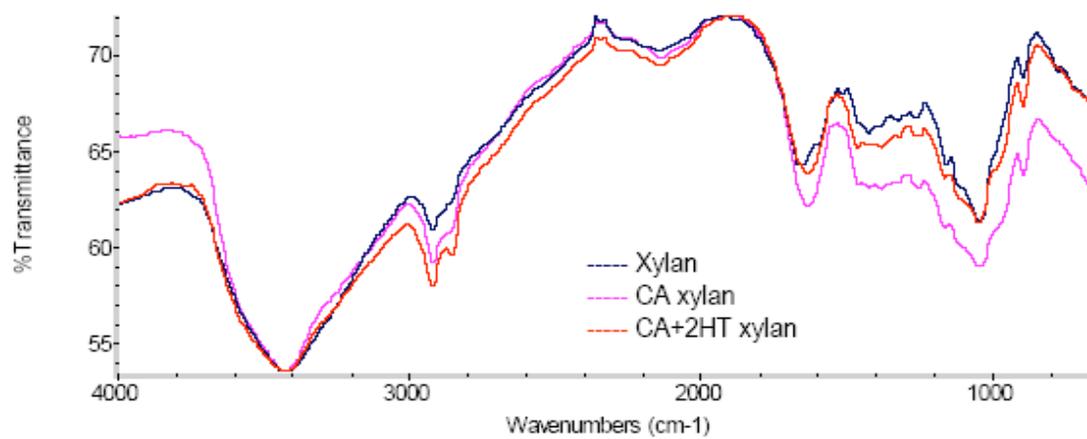


Figure 5.9. Comparison between FTIR spectra for untreated, CuAz and CuAz +2HT treated xylan.

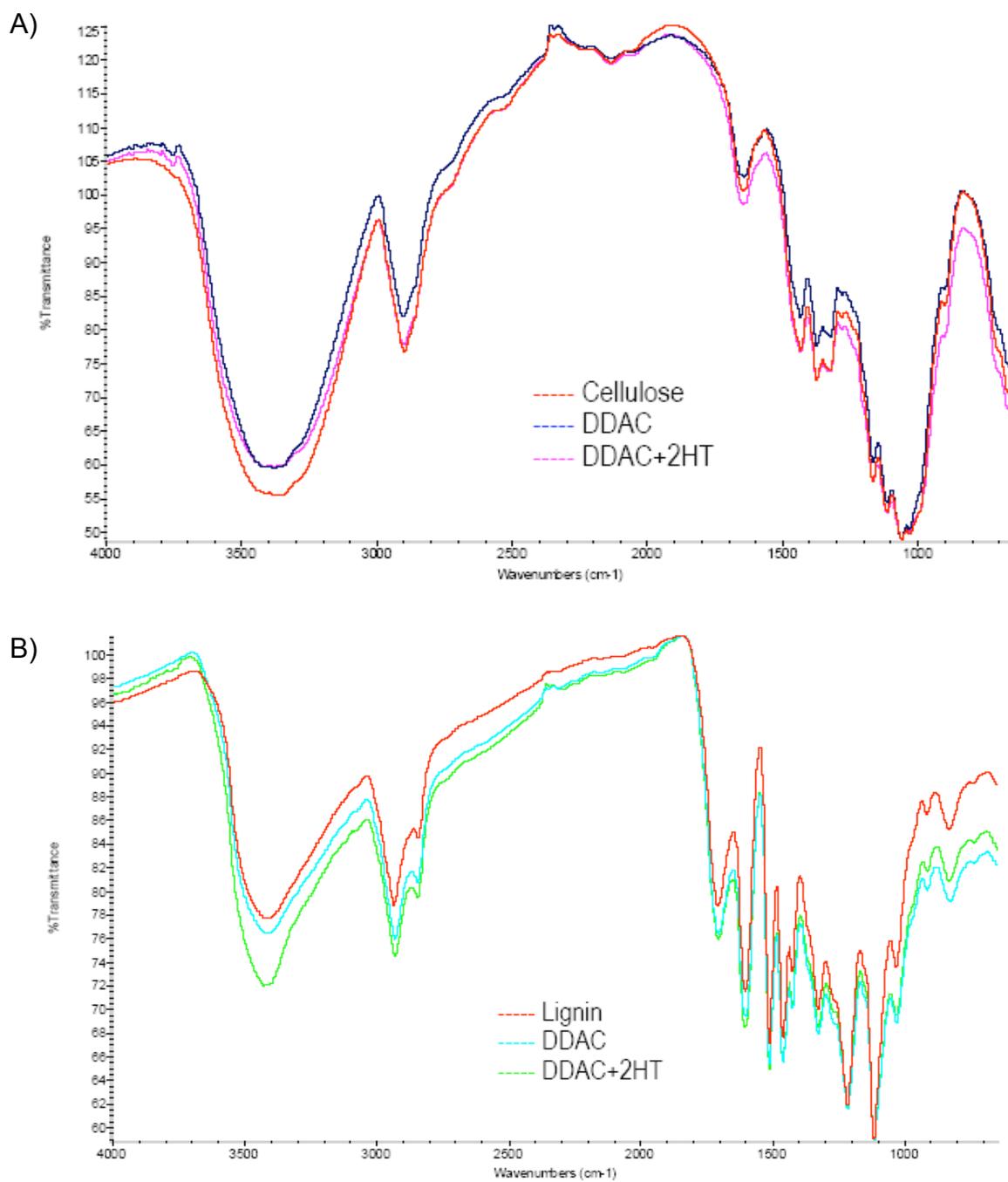


Figure 5.10. Comparison between FTIR spectra for untreated, DDAC and DDAC+2HT treated A) cellulose and B) lignin.

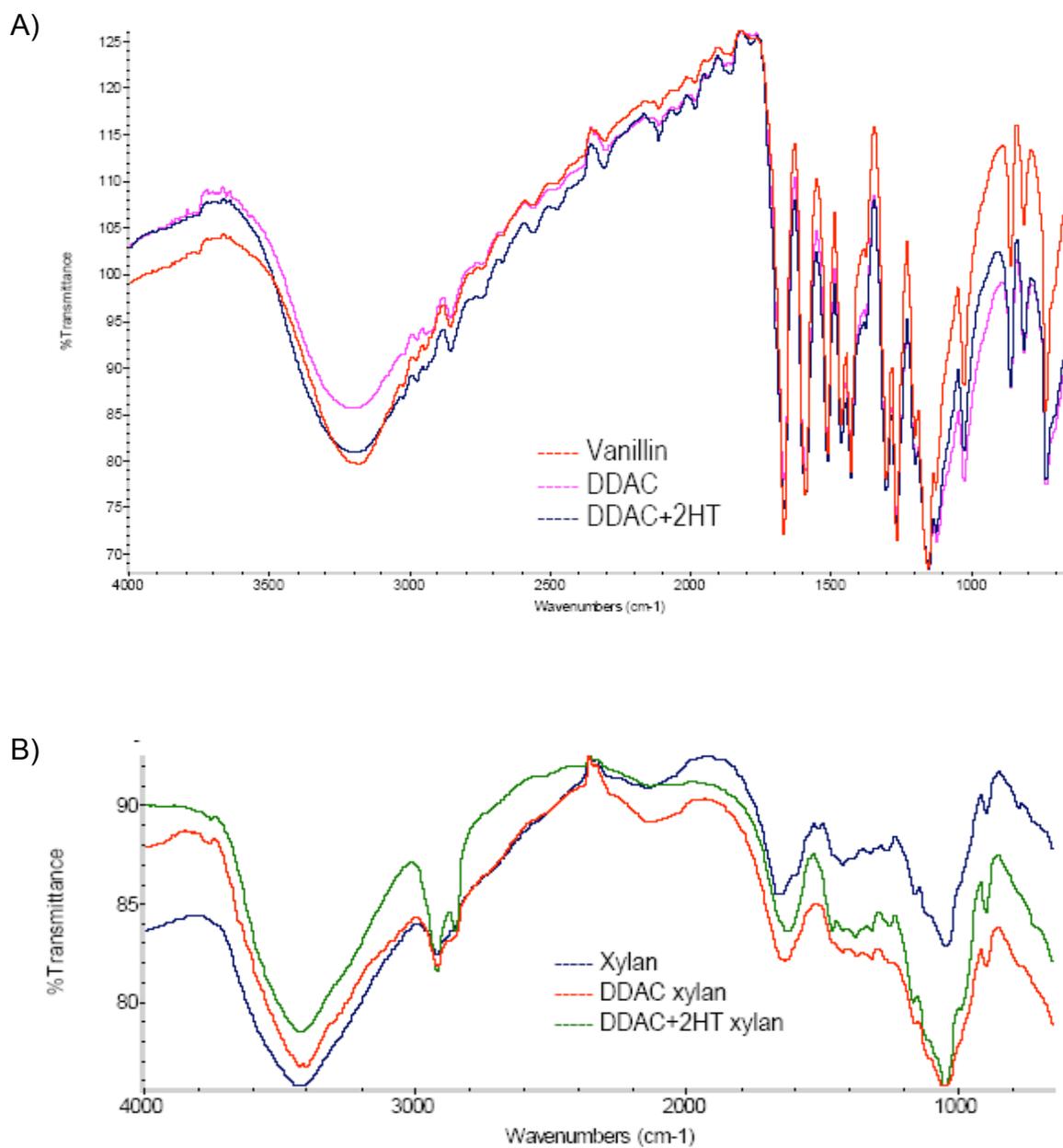


Figure 5.11. Comparisons between FTIR spectra for untreated, DDAC and DDAC+2HT treated A) vanillin and B) xylan.

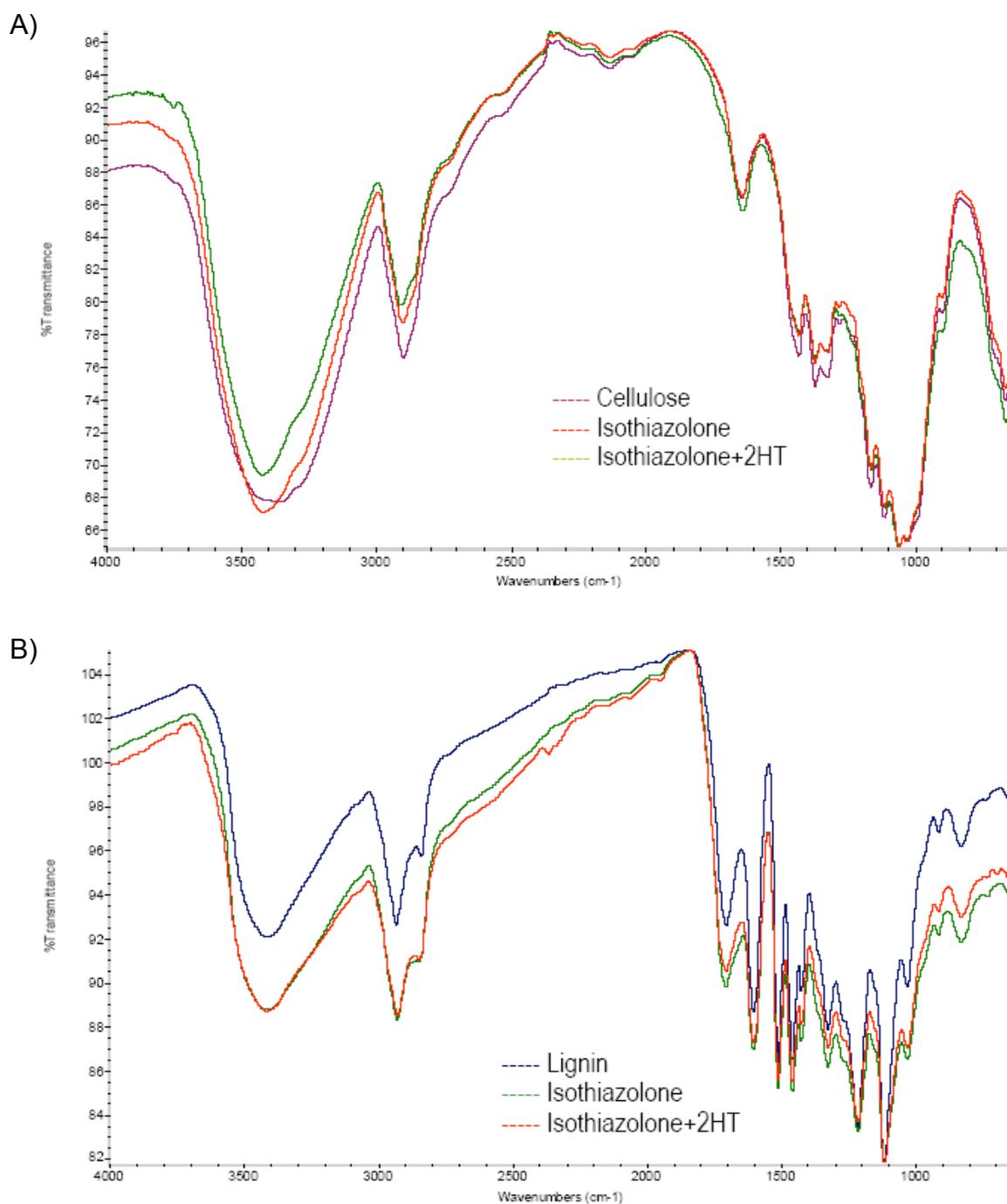


Figure 5.12. Comparisons between FTIR spectra for untreated, isothiazolone and isothiazolone+2HT treated A) Cellulose and B) Lignin.

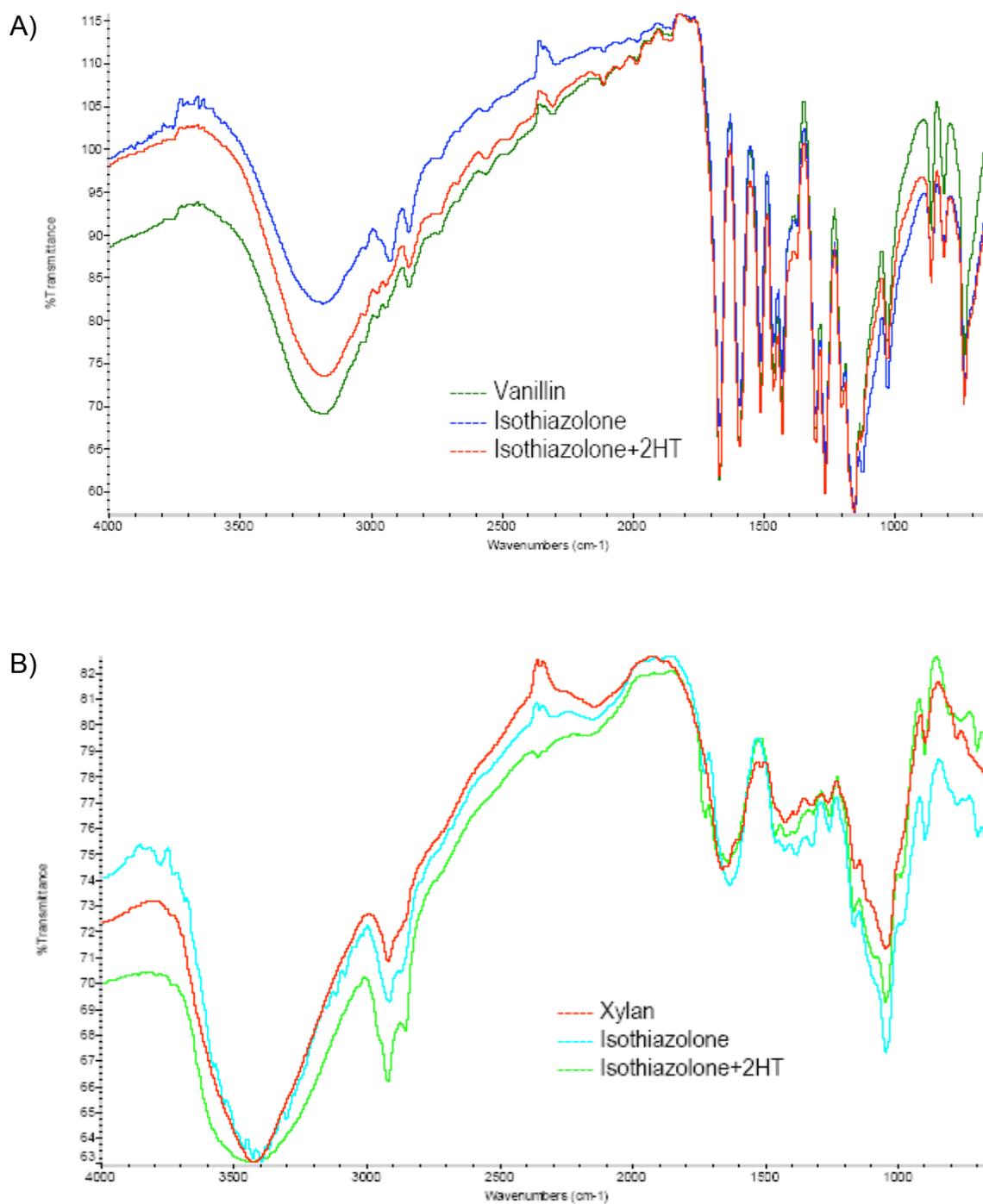


Figure 5.13. Comparisons between FTIR spectra for untreated, isothiazolone and isothiazolone+2HT treated A) vanillin and B) xylan.

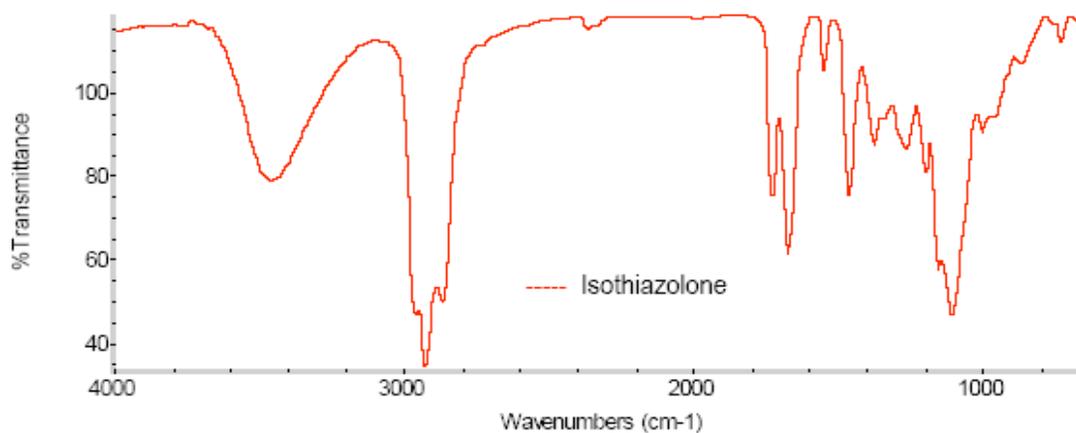


Figure 5.14. FTIR spectra of isothiazolone.

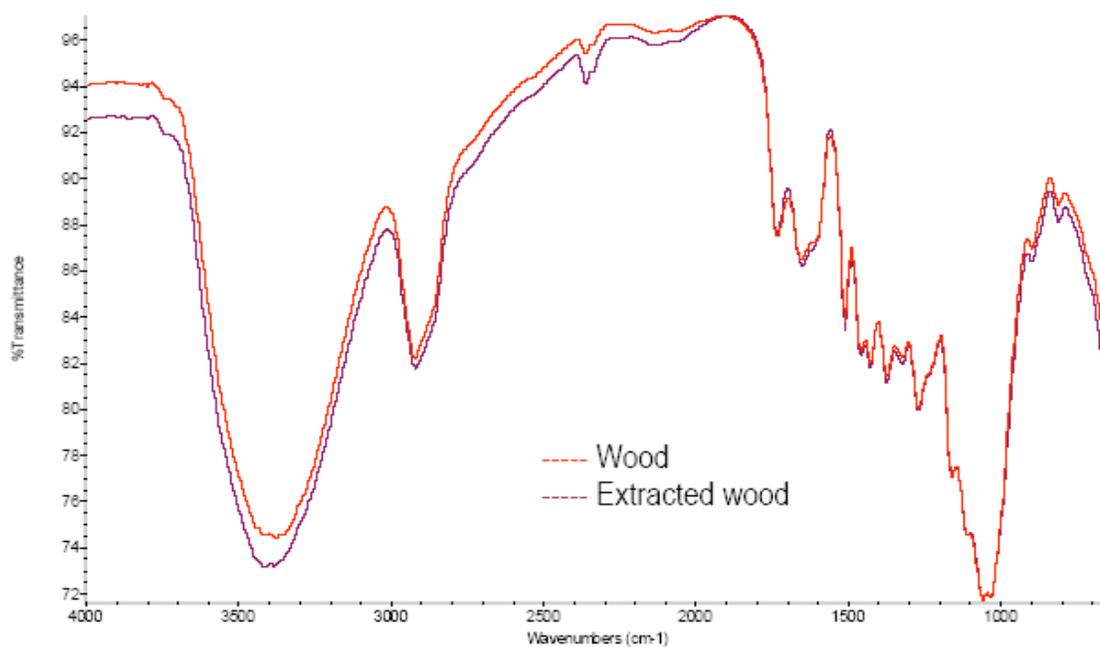


Figure 5.15. Comparisons between FTIR spectra for extracted and non-extracted wood.

CHAPTER 6 – GENERAL CONCLUSIONS

Incorporation of 2HT to alkaline copper-based preservative solutions reduced the rate of copper migration from southern pine blocks subjected to laboratory leaching procedures by 5% to 14%. 2HT had no effect on loss rates for the organic preservative, isothiazolone, suggesting that 2HT may only be useful as an additive with metal-based systems. The results suggest that 2HT may have promise for slowing copper losses into the surrounding environment.

2HT did not enhance the biological efficacy of alkaline copper compounds or isothiazolone in standard laboratory trials with the brown rot fungus, *P. placenta*. The lack of effect in laboratory trials was perplexing but may reflect the fact that the copper levels tested were already largely at or above the threshold for copper effectiveness.

Studies to assess possible chemical interactions between wood components and 2HT indicated that 2HT did not interact to any extent with the initial treatment chemicals. The results suggest that 2HT reduced copper losses because of ionic interactions between the organic cationic end of the quaternary ammonium compound and the negatively charged wood surface. This interaction leaves the hydrophobic end of 2HT exposed to act as a water

repellent, thereby excluding water that would otherwise solubilize and remove copper from the wood.

The results suggest that 2HT slows copper losses from wood treated with a number of alkaline copper systems primarily by enhancing water repellency. Further studies are suggested to assess the effects of this water repellency on long term efficacy.

Implications

The global shift towards the use of safe and environmental friendly wood preservatives has limited the use of systems such as CCA. While alkaline copper systems such as ACQ and CuAz are good alternatives, questions about leaching have arisen when wood treated with these systems is used in or near aquatic environments. While wood preservatives represent a relatively minor anthropogenic source of copper in comparison to emissions from marine vessels or car brake linings, it is also important to recognize the need to minimize the environmental impact of all materials.

An additional benefit of compounds such as 2HT is the potential to simplify management of treated wood products at the treatment facilities. The EPA has set limits on the amount of copper that treating plants can release

into the environment. 2HT could reduce leaching of preservative components from wood stored after treatment. Treating plants located in areas with constant precipitation are especially prone to leaching problems because treated wood is often stored outdoors. The incorporation of 2HT to copper-based preservatives could reduce the amount of copper released into the environment in these situations.

Opportunities for further research

This research has provided some useful information on the attributes of 2HT as an additive to limit copper losses for ACQ and CuAz systems; however, much remains unknown about the effect of 2HT on copper formulations. It would be useful to repeat the leaching and decay resistance study to include amine copper and an acid copper formulation to assess the effect of the absence of the quaternary ammonium compound competing for reaction sites.

Although FTIR analysis showed that 2HT did not react with wood, other methods for detecting 2HT complexation with wood should be considered. Some possibilities could be obtaining nitrogen maps by using an electron microprobe analyzer or by X-ray micro-analysis (SEM-EDX). It would also be

useful to expand the decay resistance study to include other types of fungi or field trials.

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