An Investigation into the Potential of Ionic Silver as a Wood Preservative

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Abstract

On December 3 1, 2003, the wood preservation industry, in conjunction with the Environmental Protection Agency, voluntarily phased out the use of chromated copper arsenate (CCA)-treated lumber for residential applications. This ended over 25 years of CCA as the predominant wood preservative in the United States. The first generation of replacement preservatives, alkaline copper quats (ACQ) and copper azole (CA), has begun to replace CCA in 2004. Other potential replacements for CCA are under investigation at the Forest Products Laboratory (FPL). One of these, recently mandated by the 108th Congress, is the use of wood preservatives based upon silver (Ag) instead of copper. Silver has been shown to have potential as a viable, safe, and cost-effective preservative. The FPL has initiated a feasibility study of ionic silver salts for inhibition of brown-rot fungi, termite damage, and mold contamination. To date, two silver formulations (~ 1% Ag) have been shown to be moderately resistant to brown-rot decay, to inhibit termite damage with 100 percent mortality of termites, and to resist colonization by three common mold species. Additional testing, including American Society for Testing and Materials leach testing and lower silver concentrations, further explore the potential of silver-based biocides as wood preservatives. We conclude that potential silver-based biocides should be investigated further to determine minimum inhibitory concentrations for fungal decay and termite damage.

Introduction

The wood preservation industry is currently in transition. As of December 31,2003, the most used preservative in history, chromated copper arsenate (CCA), has no longer been available for most residential applications. This is due to health concerns about the environmental toxicity of arsenic (As) and chromium (Cr-IV), two of the main components of CCA (1). Of primary concern is the possibility of increased cancer risk for children playing on CCA-treated playground equipment.

The currently approved substitutes for CCA, such as alkaline copper quat (ACQ) and copper azole (CA), rely on much greater levels of copper to combat attack by decay fungi and insects (1). Although these high copper systems have relatively low mammalian toxicity, there is some concern that copper, quaternary ammonium salts, and azoles may be harmful to aquatic biota. A preservative that minimizes toxicity concerns for both mammals and non-mammals would be preferable. One possibility is a wood preservative using low levels of silver.

This paper outlines the findings of a preliminary study on the feasibility of silver-based wood preservatives. It includes the results of termite feedings, leaching, boron fixation, resistance to fungal decay, and mold growth inhibition. Environmental and economic con-

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cerns of silver-based wood preservatives are also addressed.

Colloidal Silver and Ionic Silver

The most widely publicized form of silver is "colloidal silver." An Internet search on colloidal or particulate silver reveals thousands of pages filled with claims that are at best questionable and at worst deceptive. Among these claims are assertions that colloidal silver products can cure or treat over 650 diseases, ranging from cancer to diabetes (2). Others tout the antibacterial properties of colloidal silver products, claiming that they kill all microbes and none is resistant to colloidal silver (2). Little or no evidence is presented to support these claims.

Most colloidal silver products on the market use direct current on a silver electrode in aqueous solution. This is often referred to as "electrical silver." When two silver electrodes are immersed in aqueous solution and a direct current is applied, bubbles appear at one of the electrodes. This means that hydrogen in the water is being reduced and the silver electrode is being oxidized to silver hydroxide. Thus, most colloidal silver products are actually suspensions of an ionic salt.

In contrast, preparations of colloidal silver found in the academic literature were not prepared using direct current or electricity but rather were reductions of soluble silver salts, most using sodium borohydride (3-6). This very delicate and difficult process is not well-suited to mass production. This process also yields very low concentrations, because metal colloids at high concentrations tend to aggregate (7).

Perhaps the best argument against colloidal silver is the only available scholarly article on its antimicrobial efficacy. Spratt and others (8) found colloidal silver to be ineffective against bacteria when compared with more common antimicrobials such as sodium hypochlorite, chlorohexidine, and iodine. While this does not directly relate to the ability of colloidal silver to kill fungi and termites, it does offer a fair estimate of its effectiveness.

In addition, the leaching properties of a colloidal silver treatment would most likely be poor. The sizes of the particles in a silver solution tend to be in the range of 40 to 120 nm (9). These particles are too large to interact with the functional groups in cellulose or lignin, which are less than 1 nm in size (10). Therefore, the neutral silver particles would have little incentive to interact with the much smaller chemical constituents in wood (11). Also, most of the silver particles would simply be excluded by the fibrous components and not penetrate effectively, because wood has shown an ability to filter out waterborne contaminants (12). On the other hand, individual silver atoms, even uncharged, can interact with organic constituents. During redox reactions with complexed silver ions, neutral silver atoms were seen to be complexed by such ligands as EDTA (13). Reactive carboxyl groups, as found in EDTA, are also found in many components of wood and should therefore bind individual reduced silver atoms effectively (12).

It is helpful at this point to discuss the actual properties of a colloidal solution. Metal colloids are minute clusters of neutral metal atoms that are small enough to interact with polar solvents, such as water, forming an electric double layer (7). The inner layer includes absorbed ions, which for metal colloids tend to be H^+ ions (14). The outer layer is a diffuse region in which counter ions, in this case OH^-, are distributed according to Brownian motion and electrostatic forces (7). This layer is what keeps colloids from aggregating under normal conditions. When the liquid is removed, as in the case of drying after wood treatment, the particles will combine, forming larger clusters. This will decrease the surface area and may reduce the efficacy of the silver as a wood preservative. For these reasons, colloidal silver does not appear to have great potential as a wood preservative.

Ionic silver salts appear to be a better alternative to colloidal silver. Silver ions in solution offer a greater surface area because of the fact that they are individual atoms, not clusters of atoms as seen in a colloid. This means they react more quickly and readily. Also, since ions are relatively smaller than colloidal particles, they will penetrate wood more rapidly and effectively. Although some of the silver ions used in a wood treatment will most likely be reduced, they will form very small particles that can still be bound to wood components and provide a great deal of reactive surface area. Finally, a counter ion for Ag^+ can be chosen to reduce the potential for leaching. For these reasons, it appears that ionic silver has more potential than colloidal silver as a wood preservative.

Antimicrobial and Antifungal Effects of Silver

Silver is a very effective bactericide and fungicide. The silver ion concentrations that exhibits antibacterial properties is roughly 0.1 µg/L, or 10^{-9} mol/L; the concentration for fungicidal activity is 1.9 µg/L (15, 16). Silver appears to have higher toxicity for bacteria than do more notorious antimicrobial metals such as mercury, copper, lead, chromium, and tin (17). Its mammalian toxicity, however, is relatively low. Human serum concentrations of up to 600 µg/L and urine concentrations of 1,100 µg/24 h have been observed with no clinical consequences (17). Perhaps most importantly, no mutagenic or carcinogenic activity has been reported for silver (17).

The mechanisms of the antimicrobial action of silver can be described as follows (17):

1. Silver ions form insoluble compounds in the cell wall with (and thereby inactivate) sulfhydryl groups, which are essential components of enzymes responsible for transmembranous energy metabolism and electrolyte transport. The result is a loss of fluids and electrolytes from the organisms, which dry out and die.
2. Silver ions block the respiratory chain of bacteria in the cytochrome oxidase and NADH-succinate-dehydroginase region.
3. Silver ions enter the cell and bind to bacterial DNA and bacterial spores. Silver can complex with electron donor groups that contain oxygen or nitrogen. Reversible binding of bases occurs without aggregation or disruption of the double helix structure of the cell nucleus. Intercalation of silver can lead to increased stability of the double helix.
4. Silver ions in low concentrations may penetrate a bacterial cell and cause structural damage to the cell envelope. Upon entering the cell, the molecule may dissociate, after which the silver binds to the DNA.
5. Metal ions, particularly silver, can also bond to phosphate groups, forming a positive dipole on the phosphate, followed by formation of a cyclic phosphate and cleavage of these molecules at the phosphodiester bond.
6. Silver DNA complexes occur at bases, which cause denaturation by displacing hydrogen bonds between adjacent nitrogens of purines and pyrimidines, thereby preventing replication.

Note that all these mechanisms relate to solvated silver ions, Ag^+. The antibacterial properties of any metal come from its ions, which are generated from the neutral metal (1 5). In the presence of oxygen, metallic silver can be bactericidal because silver (I) oxide is soluble enough to release free silver ions (18). When dealing with metallic silver, though, it is important to note that antimicrobial activity depends on the extent of the active silver surface (19). Even if all the silver ions in a wood treatment were to be reduced to silver metal, there would still be a great deal of surface area to provide anti-microbial protection. However, after treatment and drying, both insoluble silver salts and bound silver metal are likely to be present in significant amounts. To determine the actual proportions will take further study.

Interaction of Silver Treatments with Termites and Decay Fungi

The digestive systems of termites contain protozoa that aid in the breakdown of cellulose into more easily metabolized carbohydrates (20). Because of its antimicrobial properties, silver has the potential to dispose of these organisms in the termite gut, disrupting the digestive cycle and resulting in the death of the insect. This would require the release of silver ions, which come either from the ionic salt used in the treatment or from oxidized silver metal. The solubility of the salt will most likely determine the efficacy of the treatment as it applies to termites, although all the silver salts in the treatments discussed in this paper would probably provide adequate ion concentrations for antimicrobial action.

Wood decay fungi have been shown to be susceptible to silver ions in previous studies. Silver ions in solution inhibited the activity of their cellulase enzymes (21). Wood decay fungi feeding on a block treated with silver halide would likely release more silver as a result of oxidative Fenton reactions during the breakdown of cellulose (22):

$$Fe^{2+} + H_2O_2 \text{ -- } Fe^{3+} + OH^- + HO\cdot$$

These reactions produce both hydrogen peroxide and hydroxyl radicals, which are very reactive chemicals. They are powerful oxidizing agents, much like bleach, or nitric acid (23). If a silver halide salt were used as the final product of a wood treatment, the halide anion (for example, Br^- or I^-) could interfere with this mechanism by reacting with hydrogen peroxide, the hydroxyl radical, or the superoxide radical, which may be the precursor of hydrogen peroxide in the Fenton reactions (22). The oxidation of bromide and iodide by hydrogen peroxide is an energetically favorable and kinetically realistic reaction, although it would go faster for iodide than bromide (11, 23). Both the speed and the preference for the iodide over the bromide are due to the fact that iodide ions are larger and more electron rich than are bromide ions. The products of such a reaction would be either iodine or bromine, according to the following reaction, where X denotes bromine or iodine:

$$2AgX_{(s)} + H_2O_{2(aq)} + 2H^+_{(aq)} \text{ -- } 2H_2O_{(l)} + X_{2(aq)} + 2Ag^+_{(aq)}$$

There are two important results from such a reaction. First, the molecular halogen is released. Both Br_2 and I_2 are effective biocides, which may enhance the preservative's efficacy. Second, the insoluble silver salt has been turned into free silver ions. The counter ions in this case would most likely be oxalate or hydroxide, but neither of these binds silver strongly enough to negate its biocidal properties (10). Thus, the toxic silver ions would not be released in any appreciable amount until the decay process had already begun. Once the decay fungi have been killed, the amount of released silver would decrease substantially. Such a capacity to release silver ions only when they are needed is a very attractive potential characteristic. It should be noted that this mechanism as it applies to wood preservation is only theoretical at this point, since anticipating the reactivity of such a chemically diverse environment as wood is difficult. Also, it is unknown at this point what concentrations of silver ions are necessary to inhibit decay fungi.

Binding of Silver Treatments to Wood

One certain result of a silver-based treatment of wood would be a significant amount of reduced silver, most likely on the exposed surfaces of the wood. All silver halide salts, except silver fluoride, undergo a process known as photoreduction (24). When a silver salt encounters visible light, the silver ion is reduced to the metal and the halide is oxidized to the halogen:

$$AgX_{(s)} \text{ -- } X_{2(s)} + 2Ag_{(s)}$$

This reaction is the basis of the photographic industry, which typically uses silver bromide (24). The colorless salt becomes darkened, and when the incident light is properly focused, an image will be produced. Therefore, the surfaces of silver-treated wood, especially those in direct sunlight, would become darkened, due to the presence of silver particles.

This reaction would be accelerated by the presence of more easily oxidized chemical species, such as the reducing ends of cellulose in wood. Indeed, silver ions do not even need the presence of light to be reduced in wood, because they will oxidize aldehyde groups, as found in some sugars, very readily (25). Silver has also been shown to oxidize hydroquinones, which are similar to some of the phenolic compounds found in wood, resulting in increased concentrations of unleachable silver particles (24). In addition, hydroquinone has been identified as a reactant in Fenton chemistry, providing another opportunity for silver ions to interfere with wood decay fungi (26).

The result, as previously discussed, is an organic matrix, composed mainly of cellulose, with extremely small particles of silver metal. Interestingly, an analogue of such a system already exists in the medical community, the Erlanger Silver Catheter. This device was designed to prevent infections that commonly occur with the use of catheters (19). The silver is dispersed in the polymer matrix (polyurethane) in the form of particles 20 to 80 nm in size, and the concentration of silver in the catheter is approximately 18 µg/L (16). Silver metal resulting from a wood treatment would most likely be more concentrated and smaller in size, providing more surface area and greater biocidal properties. The Erlanger Silver Catheter has been shown to be effective in reducing bacterial adhesion and proliferation (19). Although cellulose does not have the amide groups present in polyurethane, it should still provide adequate binding while sustaining an active surface. This also relates to the leachability of silver, because reduced silver in an organic matrix placed in highly vascularized tissue retains its antimicrobial efficacy.

The binding effects of the woody substrate should be very similar to those seen in the cell walls of marine algae. Both are composed of cellulose, and the form of silver in the algal membranes would be a silver halide salt, silver chloride, which would behave very similarly to the treatments used in this study. After ultrasonic disruption, washing at pH 2.0, or treatment with digestive enzymes, no silver was released from the cell walls of marine algae containing silver chloride particles (18). Thus, cellulose in timber should provide a solid binding platform for silver treatments.

Environmental Concerns of a Silver-Based Wood Preservative

A great deal of investigation has been done on the toxicity of silver ions and complexes to marine animals. Some of the findings have been rather troubling. For a wide variety of fish, the 96-hour 50 percent lethal concentration (96-h LC50) of silver ions lies in the range of 5 to 70 µg/L (27). For Daphnia magna, the 48-hour LC50 of free monovalent silver ions is 0.6 to 55 µg/L (28). Although this is more than twice the 48-hour LC50 of copper, which is still the primary biocide of ACQ and CA, it is still much lower than for experimental preservatives such as naphthaloylhydroxylamine (NHA), which has a 48-hour LC50 of 3,240 µg/L for organisms similar to Daphnia magna (29). The available data indicate that chronic silver toxicity to freshwater aquatic life may occur at concentrations as low as 0.12 µg/L (30). It is troubling that such low concentrations of silver can be lethal to aquatic life. Because of the available data that strongly suggest that complexed silver is far less toxic than free ionic Ag^{++}, these studies (27-30) were conducted in pond water, in naturally hard spring water, or in synthetically prepared hard water.

However, the ionic forms of silver evaluated in LC50 tests probably exaggerate actual environmental risks. The reasons for this are very similar to the reasons why ionic silver and copper are effective antimicrobials: they bind very strongly to a variety of ligands. After this binding occurs, the toxicity of silver drops very rapidly. For example, silver sulfide and thiosulfate complexes exhibit 96-hour LC50 values 15,000 to 20,000 times greater than that of free silver ions (31). Silver chloride complexes are at least 300 times less toxic than free silver ions, and some studies show them to be 11,000 times less toxic (18, 31). It is important to note, however, that silver chloride complexes form only at high chloride concentrations, such as are found in the oceans, and at lower chloride concentrations, insoluble silver chloride is the dominant species (32). Particulate silver chloride, as would form in brackish waters, is virtually nontoxic (18). Silver chlorides in freshwater, which are insoluble, exhibit no observed toxicity to rainbow trout (31). Even when free silver ions are introduced in a freshwater environment, the fraction of silver present as free silver ions is often less than 40 percent of the total dissolved silver concentration (27).

Like copper, silver released into natural waters rapidly becomes attached to and ameliorated by sediments. One kilogram of dry lake sediment has been shown to absorb and detoxify 2.2 g of silver ions (33). A study on the aquatic larvae of the dipteran *Chironomus tentans* showed 10-day LC50 values 275 times greater for sediment tests than for water alone (33). Studies with freshwater oligochaetes exposed to silver sulfide-spiked sediments for 28 days showed virtually no accumulation of silver from the sediments (1 8). In a test done on sediment from a Wisconsin lake, a solution of silver nitrate was mixed with soil for 29 days. Over this period of time, the decrease from the first measured silver concentration in the water to the last was 99.4 percent (33).

Environmental concerns become less threatening when considering silver leached into soil. A large portion of treated wood is used for decking–any silver from that source would need to travel through the soil and the water table to reach an aquatic environment. Because of its reactivity, silver does not migrate easily through the water table. One study reported that more than 94 percent of silver released in the environment remains in the soil or sludge at the emission site (1 8). It should be noted that this relates to dumping of soluble silver complexes from photographic chemical plants, and the proportion of bound silver in the soil would most likely be higher if it were initially insoluble or released in lower concentrations, as would be the case in wood preservation.

Another environmental concern, in addition to straightforward acute and chronic toxicity, is biomagnification, the increase in biological concentrations of harmful chemicals as one goes up the food chain. This is important because organisms at the bottom of the aquatic food chain – algae – show an extraordinary accumulation potential for dissolved heavy metals, particularly silver (18). However, biomagnification of silver in herbivorous crustaceans is unlikely, and in fact, there is no evidence of substantial biomagnification of silver in aquatic organisms (1 8). In addition, there is little evidence of bioaccumulation of silver in mammals (18). In contrast to lead or mercury, there is no evidence that silver is a biocumulative poison (34). In addition, it is possible that a silver-based preservative will be effective at much lower concentrations than those currently used for copper in the CCA alternatives. Use of lower concentrations should further reduce potential environmental impacts.

Toxicity from the treated timbers themselves should also be relatively low. Insoluble silver salts that get on human skin can simply be brushed or washed off with no effect. Even soluble silver salts that get on human skin cause only a temporary, localized darkening of the skin or nails that vanishes within 2 weeks. Silver products and silver in general do not appear to be carcinogenic (35). The risk of harm to children playing on treated wood and then licking their hands would be less of a concern for a silver-based treatment than for CCA because silver has much lower toxicity than arsenic.

There may be some serious concerns about the rare skin discoloration disease argyria. This is a cosmetic condition resulting from ingestion or inhalation of silver salts that causes darkening of the skin and eyes (36). While it poses no serious health risk, the condition is completely irreversible (36). However, the minimal oral dosage required to cause systemic argyria has been estimated to be about 25 to 30 g over 6 months (24). Considering that most silver is not absorbed by digestion, a person would need to ingest a large volume of treated wood to receive this dose (1 7). This disease should not be a pressing concern.

Potential Treatments

Silver halide salts are an attractive option for a silver-based wood preservative. The exception is silver fluoride, due to its high solubility and the possible environmental risk posed by fluoride ions. Silver halide salts are very insoluble, undergo redox reactions in the presence of light to further prevent leaching, and, in the case of bromide and iodide, provide additional biocidal activity.

The difficulty in using these chemicals arises from the same property that makes them very unlikely to leach out of wood: They are very insoluble in water. This difficulty must be overcome if they are to be used effectively. Were it not for the single issue of leachability, an excellent wood preservative would have been found decades ago in the form of water-soluble borates.

Silver cations form very insoluble salts with many common anions. Some examples are hydroxide, sulfide, oxalate, oxide, chloride, bromide, and iodide.

Among these, chloride, bromide, and iodide are the most attractive because they are not soluble in strong acid, and therefore acid rain would not promote leaching. Solubilities are as follows (23):

Salt	Saturated concentration (mol/L)	Saturated concentration (% by mass Ag^+)
AgCl	1.34×10^{-5}	0.000145
AgBr	7.21×10^{-7}	0.00000778
AgI	9.11 × 10–9	0.0000000983

Metal ions in solution are very electrophilic, meaning they are strongly attracted to lone electron pairs, and will often form complex ions with other chemical species. A good example of this is the silver-ammonia complex, $[Ag(NH_3)_2]^+_{(aq)}$, formed by the following reaction (9):

$$Ag^+_{(aq)} + 2NH_{3(aq)} \rightarrow [Ag(NH_3)_2]^+_{(aq)}$$
$$K_f = 1.6 \times 10^7$$

With such a high formation constant for this complex, we can start with silver chloride and in a 12*M* ammonia solution achieve a 6.3 percent w/v concentration of Ag^+. If silver is an effective preservative, this concentration will be well above the amount needed to prevent decay and termite damage. After treatment, the ammonia can be forced out through a combination of high temperature (80°C to 100°C), aeration, and vacuum. Thus, what remains when the treated timber reaches the consumer are only wood and insoluble silver chloride, whose leaching rate is very low. This is the simplest and most practical method of silver-based wood treatment, with a low leaching potential.

Ammonia-based treatments are promising for silver chloride, but the other silver halide salts are more difficult to get into solution. Because of the strong affinity of Br^- and Ag^+ for each other, a 12*M* ammonia solution can, at most, have only 0.38 percent w/v of Ag^+. Residual ammonia in the wood would likely cause problems because it would corrode galvanized steel fasteners as in some formulations of ACQ-treated wood. More expensive stainless steel, ceramic-coated, or galvanized-coated fasteners must now be used.

Thus, silver bromide should be less leachable than silver chloride, but treatment solutions require more ammonia, resulting in a higher pH and more cost. Also, the amount of silver that can be retained by the wood is much less because the concentration of silver is much lower.

Upon photoreduction, silver bromide may release bromine, a compound known to cause damage to the ozone layer (37). This problem may prevent the use of a bromide salt as a wood preservative, because the original goal for a silver-based wood preservative is a compound that is environmentally benign. On the other hand, bromine may react with the olefins in wood, such as terpenes, to prevent significant release into the environment (38). Further studies would be needed to determine the amount of bromine released from such a treatment.

Silver chloride and silver iodide thus seem to be the best choices. The chloride salt does have one major disadvantage. Silver chloride is insoluble but can form soluble argentate complexes with aqueous chloride ions, $[AgCl_4]^{3-}$ for example. Therefore, timber treated with silver chloride would experience significant leaching in any water with high chloride concentrations, such as seawater. This treatment may be less efficacious as a wood preservative in a marine environment. In addition, the use of calcium chloride as a de-icing agent on many roads in the winter will add to localized chloride concentrations in temperate climates, increasing the likelihood for leaching.

Silver iodide then seems the logical choice. Its anion is fairly common and somewhat benign. Its leachability potential is lower than that of any other silver halide, and it is more readily photoreduced, further decreasing its leaching potential (24). In addition, silver iodide crystals form opaque outer layers upon photoreduction (24). This may prevent significant discoloration of the wood due to particles of $Ag^o_{(s)}$. In addition, there is some evidence for silver iodide undergoing a self-redox reaction on cell membranes. Petkau and Chelack (39) found that when silver ions and iodide ions were placed on opposite sides of a phospholipid bilayer, the iodide ions were oxidized to triiodide and the silver ions were reduced to metal that formed a thin coating on the bilayer. If this took place in wood cells, it would reduce leaching potential while retaining a large amount of surface area to maintain biocidal effects.

Silver iodide does have a major drawback it is insoluble in water or concentrated ammonia to any appreciable degree. There are two ways to overcome this obstacle. Either a two-stage treatment is necessary, or the iodide must be generated in-situ. Two-stage treatments are undesirable as they add costs at the industrial level. For the purposes of this project, a combination silver nitrate/sodium periodate/sodium thiosulfate treatment was used (see description of treating solutions under Materials and Methods). It was hoped that the periodate would react with the thiosulfate to produce iodide, but determining the extent of this reaction was beyond our capabilities. For clarity, this treatment is referred to as "silver iodate."

Materials and Methods

Treatment Process

All wood treatments were done in a Pyrex desiccator. southern yellow pine (SYP) samples (feeder blocks or 3/4- by 3/4 by 3/4-in. to be treated were placed under 20 to 25 in Hg (67.5 to 84.4 kPa) of vacuum for a period of no less than 20 minutes and then immersed in the treatment solution. Immediately after immersion, the pressure was slowly raised to atmospheric over a period of 5 minutes. According to ASTM/AWPA standards, the samples were kept in the treatment solution for 30 minutes, and then wet weights were recorded. CCA, NHA, and ACQ blocks were treated to 0.4 lb./ft^3 (6.4 kg/m^3).

Treating Solutions

- Silver nitrate: 3.15 g $AgNO_3$ was dissolved in de-ionized water to give a clear and colorless solution with a final volume of 200 mL. This solution is 1 percent w/v $Ag^+_{(aq)}$.
- Silver chloride-ammonia complex: 30 mL of 28 percent w/v NH_3, 1.10 g NaCl, and 3.15 g $AgNO_3$ were combined and diluted in de-ionized water to give a clear and colorless 1 percent solution with a final volume of 200 mL.
- Silver thiosulfate complex: 5.89 g $Na_2S_2O_3$ - 5 H_2O and 3.15 g $AgNO_3$ were dissolved in de-ionized water to give a clear, light-brown 1 percent solution with a final volume of 200 mL.
- Sodium periodate/silver thiosulfate solution: 8.16 g $NaIO_4$, 3.15 g AgNO3, 9.34 g $Na_2S_2O_3^{-5}$ H_2O, and 5.1 mL 28 percent w/v NH_3 were combined in de-ionized water to a final volume of 200 mL, yielding a clear, tan-colored 1 percent solution.

In each of the following two-stage treatments, samples were first treated with a silver-precipitating agent (sodium chloride, potassium bromide, etc.), dried at 80°C for 24 hours, and then treated with a 1 percent w/v $Ag^+_{(aq)}$ solution:

- Sodium bromide solution: 1.91 g NaBr was dissolved in de-ionized water to give a clear and colorless solution with a final volume of 200 mL.
- Potassium iodide solution: 3.08 g KI was dissolved in de-ionized water to give a clear and colorless solution with a final volume of 200 mL.
- Sodium benzoate solution: 2.67 g $NaC_7H_5O_2$ was dissolved in de-ionized water to give a clear and colorless solution with a final volume of 200 mL.
- Sodium dioctaborate tetrahydrate (DOT) solution: 30.00 g DOT was dissolved in de-ionized water to a give a clear and colorless solution with a final volume of 1 L.

Treated feeder blocks (1.6 by 1 by 0.1 in.) were dried for 24 hours at 80°C and re-weighed; 3/4-inch cubes were dried for 48 hours. All blocks treated with an ammonia-containing solution were subject to 25 inHg (84.4 kPa) of vacuum while still hot after drying. In a later study to determine boron retention, the NHA/DOT and Ag/DOT combination treatment solutions were saved and analyzed for boron content lost during the second stage of treatment.

Leaching Studies

ASTM leach tests were performed on both silver-treated blocks and boron-treated blocks to determine preservative retentions. For the boron retention leaching study, four 3/4-inch cubes were placed in jars, weighed down with rubber stoppers, and immersed in 150 mL de-ionized water and agitated. Samples were to be taken at 6/24, and 48 hours and every 48 hours afterward. Unfortunately, during the 6-hour sampling phase of the 7-day leach study, a fire in another area forced an evacuation of the building. The leach jars stood, unagitated, for 18 hours before the samples were taken. The validity of the study still holds, however, because all jars were sampled at the same time and had experienced the same amount of agitation. Therefore, with respect to agitation, samples were taken after 6, 30, and 54 hours and every 48 hours afterward.

Leached samples were analyzed in a Dynex spectrophotometer. Fifty microliters of the sample, 50 µL of an ammonium acetate/acetic acid buffer, and 50 µL of ascorbic acid/azomethine-H indicator were combined in a 96-well plate. Some samples were too concentrated for the spectrophotometer to read. In these cases, 50 µL of de-ionized water was added to the well.

During the course of the study, it was discovered that the kinetics of the borate/azomethine reaction greatly affected the absorbencies. Therefore, the time involved in combining the indicator with the sample had a significant impact on the results. To compensate for this, a multi-tip pipette was used to inject the indicator. Each set of samples also had its own set of standards. Three identical rows of samples were made in the plate. The indicator was injected into the first row, then the row of standards, and then the second row of samples. The average of the two absorbencies then gave a corresponding absorbance that could be compared to the standards. A third row of samples was prepared without indicator to give a background reading.

Because of the strong reduction potential of silver, steps had to be taken to ensure that side reactions did not interfere with the reading. (In the future, these samples will be read by inductively coupled plasma (ICP) spectroscopy.) When silver ions encounter ascorbic acid, they are reduced to metallic silver nanoparticles.

This causes the solution to turn a dark brown. For the first six sets of samples, the silver was precipitated out using potassium iodide: This kept the silver from oxidizing the ascorbic acid. The final three solutions did not contain enough silver to interfere with the reading.

Decay Testing

Untreated (control) and treated blocks were subjected to three brown-rot fungi in a soil-block test (40) following the guidelines of AWPA Standard E-10 (41). Soil-block bottles were incubated at 27°C/70 percent relative humidity (RH) for 12 weeks. Blocks were removed, dried to constant weight at 60°C, reconditioned, and reweighed.

Termite Testing

For inhibition of termite damage, blocks were first conditioned at 27°C/95 percent RH overnight and then weighed. The blocks were then placed in soil bottles containing 1 g of *Reticulitermes flavipes* harvested from southern Wisconsin. The bottles were kept at 27°C/95 percent RH for 28 days. Afterward, the blocks were dried, re-conditioned, and weighed. The remaining live termites were also weighed (42).

The silver nitrate, silver bromide, silver chloride, and sodium periodate/silver thiosulfate blocks had experienced so little feeding that it was decided to leach them and then redo the feedings. For this study, all five blocks from one treatment were combined in one jar and immersed in 150 mL of deionized water and agitated. The water was changed and samples were taken every 24 hours for 4 days; one final sample was taken at 7 days.

Results and Discussion

The potential of silver salts to inhibit brown-rot fungal decay was determined in 12-week ASTM soil-block tests **(Fig. 1).** Silver bromide (AgBr), silver chloride (AgCl), and silver nitrate ($AgNO_3$) showed little or no inhibition of fungal decay. Silver thiosulfate and silver periodate showed modest inhibition at 1 percent concentration as compared to CCA.

Inhibition of termite damage was tested in a modified 4-week ASTM (43) test using leached and unleached sample blocks treated at 1 percent Ag concentration for each test solution. Weight loss, block ratings, and termite mortality for the various treatments are shown in **Table 1.**

The initial termite data are promising. Silver iodate, leached and unleached, compared favorably to ACQ, the predominant CCA replacement. It should be noted that the silver iodate data are somewhat ambiguous. The blocks themselves showed no evidence of termite feeding, and most termites in these bottles died within 2 weeks. The 8.72 percent weight loss in the unleached blocks was most likely due to a conditioning error. Therefore, we have at least two, and likely three, silver-based wood preservatives that have excellent resistance to termite feeding. All two-stage treatments also showed promise, performing similarly to ACQ. As discussed previously, all the blocks showed darkening except for the one-stage silver iodide treatment, which turned a light tan.

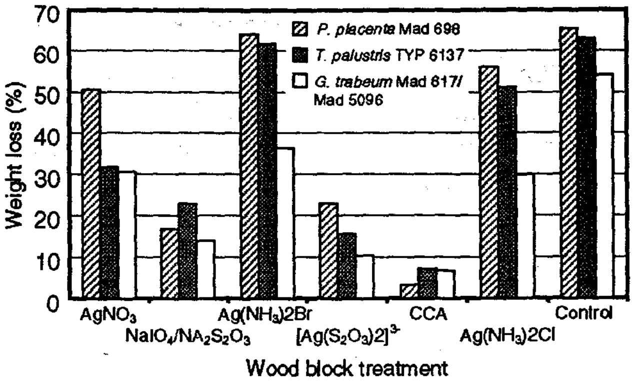

Figure 1. ~ *Inhibition of brown-rot decay fungi by silver salts compared to CCA in 12-week soil block test. Silver salts: silver nitrate,* $AgNO_3$*; silver periodate,* $NaIO_4Na_2S_2O_3$*; silver bromide,* $Ag(NH_3)2Br$*; silver thosulfate,* $[Ag(S_2O_3)2]^{3-}$ *; silver chloride,* $Ag(NH_3)2Cl$*.*

Table 1. ~ *Evaluation of termite damage to southern yellow pine treated feeder blocks.*

Treatment[a]	Mean weight loss[b]	Mean block rating[c]	Termite mortality
	(%)		(%)
Silver nitrate	(0.01 ± 0.04)	10.0	99.14
Silver nitrate (L)	4.03 ± 3.72	5.2	62.00
Silver chloride	0.46 ± 0.38	9.8	98.50
Silver chloride (L)	4.24 ± 3.45	6.2	50.08
Silver nitrate/iodide II	1.65 ± 0.44	9.8	100.00
Silver nitrate/bromide II	1.76 ± 0.45	9.4	99.92
Silver nitrate/benzoate II	2.66 ± 0.60	9.8	99.10
Silver bromide	3.29 ± 1.18	7.4	98.76
Silverbromide (L)	9.26 ± 6.56	2.8	52.64
Silver thiosulfate	4.13 ± 1.32	9.0	94.04
Silver thiodulfate (L)	17.42 ± 16.21	2	42.54
Silver iodate I	8.72 ± 1.80	10.0	100.00
Silver iodate (L) I	(1.52 ± 0.22)	10.0	100.00
ACQ	(1.78 ± 0.37)	10	99.12
NHA	0.56 ± 0.24	10	99.82
Control	22.39 ± 4.96	0	21.15

[a] (L) denotes leached block.
[b] Parentheses denote negative values (ie., weight gain).
[c] Visual rating: 10, sound; 9, light damage; 7, moderate damage; 4, heavy damage; 0, failure.

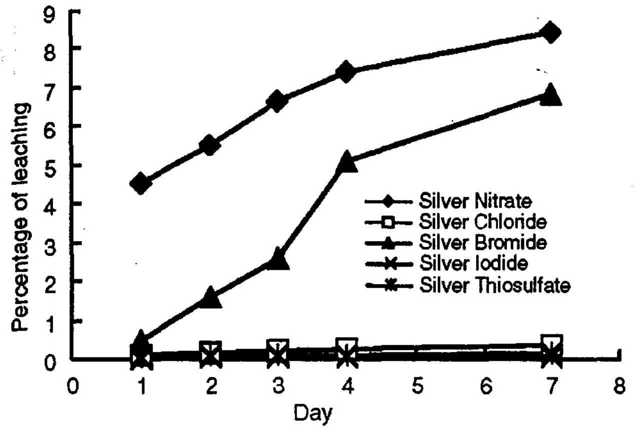

Figure 2. ~ *Cumulative silver leached from treated feeder blocks in 7-day leach study.*

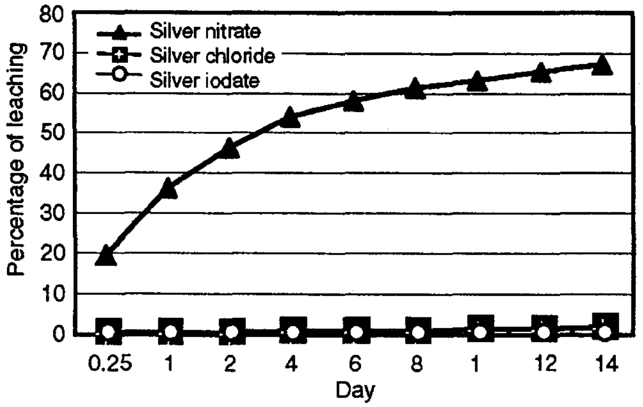

Figure 3.~*Leaching of silver from 3/4-inch blocks treated with silver nitrate, silver chloride, or silver iodate in 14-day leach study.*

Mold tests were also done for some treatments. Inhibition of mold is a difficult task in the wood preservation industry. Even the venerable borates fail to inhibit mold growth except at very high concentrations. According to ASTM standard D4445-91, a 4-week dip test for mold inhibition was performed, but only silver nitrate proved effective when challenged with three common mold fungi. This was also one of the most effective treatments for termites. It may not prove to be the preservative of choice, however, since it would likely be the most leachable based upon solubility. A second mold inhibition test was conducted using the silver iodate feeders that survived the termite testing after leaching; these feeders showed inhibition to three species of common household molds in a 4-week test. Mold inhibition by silver nitrate and silver iodate look promising, and tests should be expanded and repeated.

Some two-stage silver iodate blocks showed a partial loss of structural integrity after the termite feedings, although almost no termite attack had occurred. This may indicate some structural damage caused by the treatments and should be investigated further.

A preliminary 7-day leaching study was done on silver compounds using feeder blocks. Although the results suggest that certain silver compounds have the potential to be leach-resistant preservatives, this must be confirmed with a more thorough investigation (Fig. 2). Silver nitrate, the most water-soluble treatment, was 90 percent retained after 1 week of immersion and agitation. The other treatments did much better because the resulting chemicals were insoluble in water. Only silver bromide showed any significant leaching. The remaining silver compounds leached less than 1 percent.

In the 14-day ASTM leach test using 3/4- by 3/4-inch SYP blocks, 65 percent of the silver nitrate leached out. Silver chloride and iodate again showed resistance to leaching (less than 1%), and leached blocks still exhibited substantial termite resistance **(Table 1).** Virtually no silver was released from blocks treated with silver chloride and silver iodate **(Fig. 3).** The amount of silver released was near the lower edge of the detection limits for the apparatus used in this study. The leach resistance of silver chloride is even beyond what one would expect from its low solubility. Silver chloride must, therefore, produce a large proportion of reduced silver metal after injection into the wood. Indeed, the surfaces of blocks treated in this manner were darkened severely. This may be only a cosmetic effect, but the structural integrity of larger timbers treated with silver chloride solutions may be adversely affected. In addition, cosmetic effects cannot be disregarded when considering treated wood that is going to be sold to the general public.

The fixative power of silver for boron was also demonstrated. Silver ions and borate ions reacted to form an insoluble ionic salt, which was resistant to leaching. Previous studies had shown that the organic salt NHA also prevented boron leaching: silver seems to be a more effective agent for this process, although the standard deviations for the two curves seem to overlap. A comparison with a treatment of known leachability, such as DOT, demonstrates this potential **(Fig. 4).** Blocks treated with DOT, which were subjected to the same immersion and agitation as the other treated blocks, lost 70 percent of the preservative after just 6 hours. After 1 week, DOT was completely removed from the wood in a similar amount of time. This 10 percent standard deviation range is similar to the leachability of copper in ACQ (1). Two-step treatments of DOT with $AgNO_3$ and NHA retained 40 percent and 30 percent DOT, respectively. When these same blocks were tested against

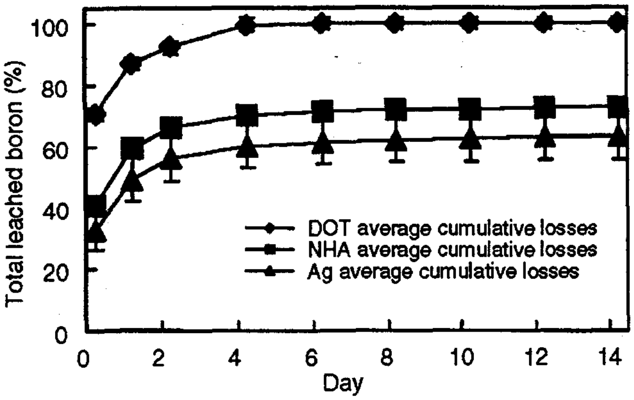

Figure 4. ~ *Retention of DOT by secondary treatment with NHA and silver in 14-day leach study.*

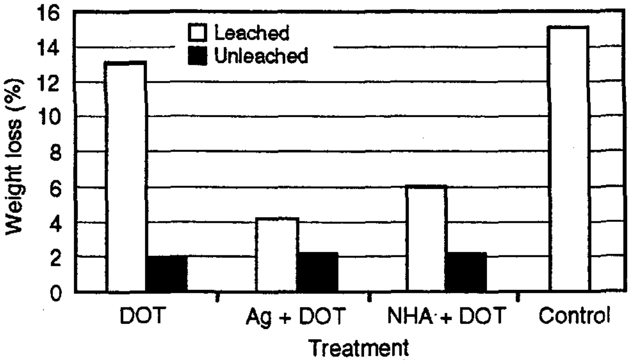

Figure 5. ~ *Resistance to termite damage of 3/4-inch leached and unleached southern yellow pine blocks treated with DO?: DOT plus silver, and DOT plus NHA.*

termite damage by *R. flavipes,* precipitation of DOT showed enhanced protection of leached blocks **(Fig. 5).**

The susceptibility of silver nitrate to leaching appears to be related to its solubility in water. Silver ions in wood, as discussed previously, will react with reduced carbon in lignin and cellulose to transform into silver metal in the form of submicroscopic silver nanoparticles. The solubility of silver metal in water is extremely low and even lower when it is bound within the organic matrix of treated wood. This fixation process is very similar to that which CCA undergoes (35). The result is a large surface area of silver metal, which may have the ability to prevent termite damage while being resistant to leaching.

Silver nitrate exhibited some interesting behavior. In its original form, it was an ionic salt that was soluble in water. After 2 weeks of leaching, two-thirds of the initial silver was released **(Fig. 3).** This provides useful data for the amount of soluble ionic silver that can be retained by wood. In addition, silver nitrate showed termite resistance similar to that of silver chloride after leaching **(Table 1).** Therefore, we can assume that the majority of silver retained in leached, silver chloride-treated blocks was not necessary in reducing termite attack. An alternative explanation would be that both the nitrate and chloride are leached out. A lower concentration in the initial treatment may result in lower leaching while retaining efficacy against termites for both silver chloride and silver nitrate.

The resistance of silver-treated wood to decay fungi was moderate to low **(Fig. 1).** Results for all treatments were worse than that for CCA-treated wood, and wood treated with nitrate, bromide, and chloride showed little to no resistance compared with the untreated controls. Again, silver iodate came out near the top, with thiosulfate doing almost as well. Silver thiosulfate treatments were less resistant to termite feeding, so silver iodate appears to be the most promising treatment against brown-rot fungi. Overall, the ionic silver-based biocides tested in this study do not provide adequate resistance to wood decay fungi.

Silver iodate/periodate seems to stand out among the various treatments tested here. At a silver treatment concentration of 1 percent, wood treated with $AgIO_4$ had relatively low fungal damage, and when compared with other silver treatments, $AgIO_4$ showed low leachability and the best termite resistance after leaching. In addition, blocks treated in this manner showed little or no discoloration. Silver iodate also showed resistance to a mixture of three common mold spores after a 4-week incubation test. The contribution of the counter ion periodate was previously described by Chen and Rowell (44). While the environmental impact of silver has been discussed, the impact of iodine has not. It is unknown how much iodine was released from these blocks during the leaching study. If iodine leaching is within reasonable limits, then the silver iodate combination treatment may have potential as a wood preservative.

Cost

With all the potential advantages of a silver-based wood preservative, its main drawback is cost. One percent by mass Ag^+ solutions as prepared in this study would cost approximately $30/gallon. A silver bromide, silver iodide, silver thiosulfate, or silver chloride-based solution would be even more expensive. However, bulk and industrial prices will be much lower. The minimum cost for a solution with anti-fungal properties would be around $1.10/gallon (15, 16). Current non-arsenate wood preservatives cost less than $5.00/pound, which translates to about $0.40/gallon. This should not be an immediate disqualifier of silver, however, because its leaching and antimicrobial potential suggests the possibility that a treatment solution of less than 1 percent w/v Ag^+ may be effective against termites and decay fungi **(Fig. 1).** The cost bar to silver-based biocides and other alternatives to CCA has been lowered because the copper-azoles and ACQ treatments are more expensive than CCA and require more expensive fasteners.

Future Research Proposals

While much data have been gathered, additional data are needed to further evaluate the potential of silver as a wood preservative. All treatments done in this study, except for the silver bromide solution (0.38%), were done at 1 percent w/v Ag^+. Further treatments and termite feedings should be done at 0.5 percent to 0.1 percent and 1.5 percent to 5 percent to determine the minimum inhibitory concentration (MIC) necessary for preservative efficacy. In addition, further leaching studies should be done. Using ICP, concentrations of several elements can be determined at once. This would be a powerful tool in determining whether the silver nitrate/sodium periodate/sodium thiosulfate (AgNPT) treatment prevents leaching of just silver or silver, iodine, and sulfur. If none of these elements leaches out, the silver iodate treatment might have a future in the industry. None of the elements used is especially hazardous to the environment, and even so, these elements may not leach out to any significant degree. This silver iodate formulation seems to have the best potential. It is an effective termiticide, and initial fungal test results show it to be nearly as toxic to decay fungi as is CCA. All treatments should be tested at lower concentrations, however, since they may have advantages that have not yet been considered. It may be advantageous to do field testing of those silver formulations that look most promising.

While several types of silver-based treatments have been studied here, there may be others that should be tried. Some may be synergistic with other preservatives. Silver nitrate treatments should be done with different types of curing. Humidity probably plays an important role in the curing process whereby silver atoms fix themselves to the wood. Comparisons should be done on blocks conditioned at various temperatures and humidities. Also, new methods of creating a one-step silver iodide treatment should be considered. One way of dissolving solid silver iodide is to add excess iodide to the solution. The problem with this is that the iodide stays in the wood and can contribute to leaching or present an environmental hazard. If the blocks were conditioned at high heat and humidity, the iodide may be oxidized to form molecular iodine, which could also fix itself to the wood. Therefore, a silver iodo-argentate complex should be studied. Thiosulfate was used in two separate treatments so far, but this should still be attempted with raw silver iodide, since it too can be oxidized during the fixation process. Other treatment options will certainly present themselves in future studies, further making the case for continued research in this area.

Conclusion

The current situation in wood preservation and the potential of a silver-based wood preservative warrant further investigation. This report examines only ionic silver salts. If silver iodate is shown to be toxic to decay fungi at lower concentrations and its mammalian toxicity is relatively low, then further study in this area is warranted. Silver iodate is also effective at preventing termite damage (leached and unleached) at a 1 percent concentration. The important factor that must be investigated is the level of treatment necessary for termite resistance and decay prevention. The leaching of silver nitrate-treated blocks shows that the 0.3 percent solutions used in this study were below the concentrations needed. Future studies should investigate silver nitrate, silver chloride, and silver iodate treatments at reduced levels. In addition, leaching tests should be done in various types of solutions, as opposed to the de-ionized water used for this study. Specifically, the leachability of silver treatments in marine waters must be investigated.

The viability of two-stage treatments should also be further investigated. There is a wood preservation industry precedent for a two-stage treatment in DDAC, but it was never commercialized due to cost. Most importantly, the leachability of silver and the biocide contribution of counter ions should be investigated.

Concerns about environmental risks are perhaps the most difficult hurdle when dealing with heavy metals. This is debatable with silver. The toxicity of silver ions is high, but silver ions are so reactive that their toxic effects in the environment may be negated. The environmental impact of silver could be minimal, especially if it is effective at lower concentrations than is copper. Silver ions that enter an ecosystem will not get far before becoming irreversibly attached to soils, clays, organic matter, or inorganic minerals. Those few silver atoms that do migrate into a water table form metal complexes whose toxicity is many thousand times less than that of free silver ions. Finally, there are no reported carcinogenic, mutagenic, or long-term effects of silver exposure.

One other disadvantage of a silver-based wood preservative may be cost. Silver metal is somewhat expensive, making silver compounds that can be turned into preservatives even more expensive. The key to silver's potential as a wood preservative is the concentration needed to protect wood. Further screening tests should be conducted to determine toxicity thresholds and the cost of the resulting successful treatments. If warranted by these laboratory trials, field stake tests with promising formulations should be initiated.

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