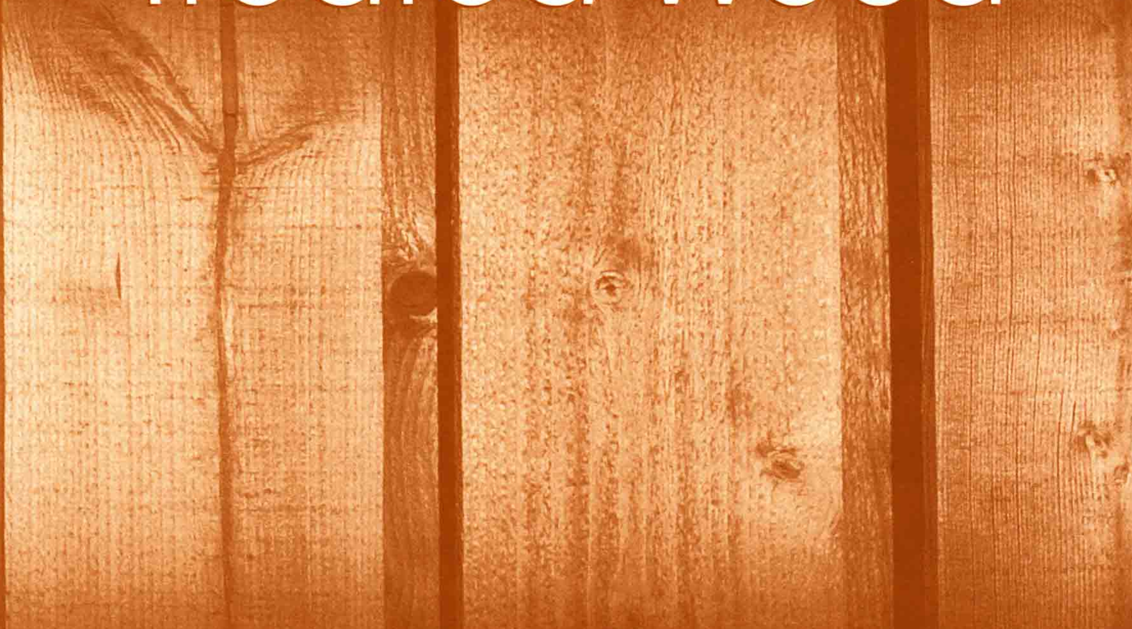
Environmental Impacts of Treated Wood



Edited by
Timothy G. Townsend
Helena Solo-Gabriele

CRC Taylor & Francis
Taylor & Francis Group

Non-Arsenical Wood Protection:
Alternatives for CCA, Creosote, and Pentachlorophenol

Mike H. Freeman[1], Darrel D. Nicholas[2] and Tor P. Schultz[*2]

[1]Independent Wood Scientist
7421 Hunters Tree Cove
Memphis, TN 38125

[2] Professors
Forest Products Laboratory, FWRC
Box 9820
Mississippi State University
Mississippi State, MS 39762-9820

[*]Corresponding Author – tschultz@cfr.msstate.edu

1. Introduction

Traditionally, the wood protection industry has relied on only a few 1st generation preservatives that have a broad range of activity, are low cost and have long-term efficacy. The three main U.S. preservatives for industrial applications are creosote, oilborne pentachlorophenol, and the waterborne arsenicals, principally chromated copper arsenate (CCA). For residential applications, the major market for treated wood, CCA was by far the major preservative up to January 2004 but is no longer labeled [permitted] for most residential applications.

Creosote is a viscous black coal-tar distillation by-product composed of a complex mixture of polyaromatic hydrocarbons (PAHs), polynuclear aromatics (PNAs) and other chemicals, and is principally used to treat railroad ties, utility poles and pilings. Creosote recently accounted for about 10% by volume of the treated wood in North America. Pentachlorophenol (penta, PCP) is an inexpensive oilborne chemical that has replaced creosote in many industrial applications, primarily used for treating utility poles and crossarms, and accounts for about 10% of all treated wood in North America. Penta and creosote are under increasing pressure in the U.S. due to possible health, environmental and disposal concerns, and many countries have restricted or outright banned creosote and/or penta. The major wood preservatives in North America were the waterborne arsenicals, principally CCA. CCA is very effective, economical, dependable, and leaves lumber with a clean and non-oily surface. Thus, in 2003 CCA accounted for about 80% of the total volume of treated wood in the U.S. and over 95% of treated lumber for residential applications. However, CCA is no longer labeled for most residential applications. CCA will still be permitted for a few residential applications, such as treating lumber in permanent wood foundations and sawn structural poles, and CCA is still labeled for industrial uses. The volume of CCA-treated wood produced will likely decrease by about 68%. [See the prior chapter by Morrell for a review on CCA] .Another arsenical is ammoniacal copper zinc arsenate (ACZA), which is used to treat some refractory species [woods in which it is difficult to achieve good biocide penetration] in western North America.

The purpose of this chapter is to discuss CCA alternatives that are commercially available, labeled but not commercially available, or being studied for possible use in the U.S., Europe and/or Asia. Specifically, we will discuss biocides that are usually dissolved in a carrier with the liquid solution then used to treat wood. These include inorganics (borates, the "new" 2nd systems which contain non-complexed copper(II) with a co-biocide, and systems which contain complexed metals [and prehaps additional uncomplexed copper]), then organic biocides (and the 3rd generation totally-organic preservatives) currently used to protect wood and organic agrochemicals with the potential to protect wood. We then briefly discuss the formulation of a biocide into a commercially-useful liquid wood preservative system, with the biocide system usually impregnated into lumber or poles by a pressure treatment process. We also discuss non-biocidal methods to protect wood, and the trends and problems with developing an effective and economical wood preservative system.

2. Inorganic Systems

2.1 Borates

Borates (borax, boric acid, disodium octaborate tetrahydrate (DOT), sodium borate, (SBX)) are inorganic boron-based biocides, generally formulated as a mixture of borax and boric acid into a waterborne system. Borates have extremely low mammalian toxicity and a broad range of activity against decay fungi and insects including the Formosan termite. They are not corrosive to metal fasteners, are colorless and odorless, paintable once the treated wood is dried and are inexpensive and readily soluble in water. However, their water solubility limits applications to those with minimal or no leaching potential. Borates, used for over 50 years in New Zealand to protect lumber, were introduced into the U.S. about 15 years ago. The major U.S. companies which supply wood preservative systems all have borate systems. These systems are generally intended for non-exposed structural applications, such as internal structural lumber studs and wood-based panels for residential construction along the Gulf Coast or in Hawaii where drywood and/or Formosan termites are present. Borates are also a co-biocide in some of the new non-arsenical copper-based systems for exterior applications, such as the CBA and CX systems discussed below, but the boron is susceptible to rapid leaching in outdoor exposure. Borates are also used as a diffusible biocide for the remedial treatment of millwork and related products/applications in many countries. Much research has been conducted to find compounds that will complex with borates, or to use water repellents, to reduce leaching, but the results so far are generally poor. Several new firms use either a dual-treatment process, with lumber treated first with a borate system followed by a second treatment with a silicate compound, or both compounds mixed together and treated followed by a fixation process. This is claimed to produce lumber suitable for exterior above-ground exposure such as decking, but as of August 2004 none of these systems have been standardized [approved] by an appropriate regulatory agency [but at least one proposal has been submitted to a standard-setting authority.]

2.2 Systems with Uncomplexed Copper

Most of the "new" systems that have replaced CCA for exterior residential applications in North America are based on the combination of uncomplexed copper [specifically copper(II), Cu(II) or cupric] to control most decay fungi and termites and an organic co-biocide to inhibit copper-tolerant fungi. These waterborne, copper-rich systems have been commercially available in Europe, Japan, and Asia for some time. The two main U.S. systems are alkaline copper quat (ACQ) and copper azole (CA). Considerable research has shown that these two systems are generally as effective as CCA for above-ground, ground-contact, and fresh water applications and they contain neither arsenic nor chromium, two metals with environmental and health concerns. Disadvantages include high levels of copper, a metal under U.S. EPA [Environmental Protection Agency] scrutiny, and a relatively high formulation cost compared to CCA due to the need for an organic amine or ammonia to react with the hydrated copper ion and form a temporary complex to minimize metal corrosion in the treating plant and improve copper penetration and distribution in the treated lumber. [Shortly after treatment the ammonia or amine will start to evaporate or leach out. Thus, these copper-based systems are only temporarily complexed, as opposed to the permanently complexed copper systems discussed in the next section.] The presence of the amine and absence of arsenic appears to enhance mold growth on wet, freshly-treated lumber compared to CCA-treated lumber, although surface molds can be controlled by adding a mildewcide to the preservative system. (Mold growth on wet CCA-treated lumber is also a common but generally unrecognized problem.) Another problem is greater metal corrosion, both in the treating plant and with metal fasteners used with the treated lumber. This corrosion is due to: 1) the uncomplexed copper ion which acts as an oxidizer to "rust" iron; 2) the absence of chromium in the newer systems [the Cr in CCA greatly reduces rusting by stabilizing the surface of iron fasteners]; and; 3) the amine present in 2nd-generation systems which removes some of the zinc protective coating of galvanized metal fasteners. Corrosion can be minimized by using appropriate fasteners and joist hangers, such as stainless steel or hot-dipped galvanized metal with three times the normal galvanic coating thickness, or screws with a ceramic or phosphate coating. However, many consumers are not fully aware of the higher corrosion potential and some metal corrosion problems with the newer systems are inevitable (litigation due to metal corrosion is already pending). The newer CCA-replacements also leach relatively high levels of copper which can have a negative impact on aquatic systems. Formulation research is currently underway to reduce copper leaching and/or fastener corrosion.

Copper azole, either with (CBA) or without added boron (CA-type B), consists principally of the biocide copper, relatively small amounts of the highly effective organic azole biocide tebuconazole, and perhaps boron. The organic amine generally used to complex with the copper is monoethanolamine, which greatly reduces corrosion problems in the treating plant but increases the system's cost. Waterborne CA/CBA is used for above-ground, ground-contact and freshwater applications in Europe, Asia, and the U.S. In the U.S., about 40% of the treating plants which previously used CCA have converted to copper azole, principally CA-B.

Waterborne alkaline copper quats (copper quats, ACQ, amine copper quat, ammoniacal copper quat) combine the biocides copper and one of the quaternary ammonium compounds (quats) discussed below, usually with a CuO:quat ratio of 2:1. These are formulated into a waterborne system using ammonia or a relatively expensive organic amine to complex with the free copper. Three types of ACQ are available in North America, with various formulations and quats for above-ground, ground-contact, and freshwater applications. ACQ has been available in the U.S. and Australia for about 12 years and even longer in Europe and Japan. ACQ is used in almost 60% of the pressure treating plants that formerly used CCA. Recent developments include the replacement of the chlorine anion in quats such as DDAC (didecyl dimethyl ammonium chloride) with other anions, principally carbonates, to minimize corrosion in the treating plants.

While ACQ and CA are the major new residential wood preservative systems in the U.S., other free copper waterborne systems are or were available in Europe and/or the U.S., or are standardized. [Standardized means subjected means to a critical and comprehensive review process by an appropriate regulatory agency following which the preservative is listed/approved for use. The major U.S. organizations involved in setting standards are the AWPA (American Wood Preservers' Association) and ASTM (American Society for Testing Materials), but about 10 other standard-setting agencies are involved to some extent.] Chromated copper borate (CCB) and related copper/chromium systems are available in Europe, but environmental concerns and disposal issues may soon limit these preservatives. In the U.S., acid copper chromate (ACC) was an older system that had not been used for residential applications for 20 years but was still listed for residential and commercial applications in the 2002 AWPA Standards. The chromium greatly reduced metal corrosion compared to the newer copper-rich systems, and ACC-treated lumber generally performed well in above-ground applications. ACC-treated lumber for residential applications was recently reintroduced for a brief time but environmental and liability issues caused the supplier to quickly remove it from the market.

2.3 Complexed Metal-Based Systems

Metal-ligand, or organometallic, systems include metals, usually copper, which are complexed with organic ligands. While the uncomplexed copper systems described above are waterborne, complexed metal systems can be either waterborne or oilborne. Additional uncomplexed copper can also be present, especially in waterborne residential systems; if free copper is present then lumber treated using these systems can have metal corrosion problems. Systems in which the copper is tightly complexed to a ligand may have less metal corrosion than lumber treated with ACQ and CA (but some carriers or additives can cause corrosion), and the relatively low metal content of some complexed metal systems may make future disposal of wood treated with these systems easier than for wood treated with the copper-rich systems.

The copper bis-(N-cyclohexyldiazeniumdioxy) preservative (also known as Cu-HDO, copper xyligen (CX)) consists of the biocides Cu-HDO, additional uncomplexed copper, and boron. The Cu-HDO portion exhibits good stability, but the borate component can leach relatively quickly and the uncomplexed copper is also subject to some leaching. Cu-HDO is one of the major waterborne systems in Europe for above-ground and ground-contact applications. Research on-going in the U.S. indicates good efficacy with above-ground samples, but poor results were sometimes observed for ground-contact samples in locations with copper-tolerant fungi. A waterborne Cu-HDO standard has just been developed by the AWPA for above-ground applications in the U.S., CX-type A, which may be available once Cu-HDO is registered by the EPA. It is formulated with an organic amine having 93.6% of the copper as free copper(II) carbonate, the remaining 6.4% copper complexed as Cu-HDO, and boric acid.

(*Bis*) copper-8-quinolinolate (oxine copper, copper-8, Cu-8) is an organometallic with very low acute mammalian toxicity, excellent stability and leach resistance, broad activity against decay fungi and insects, but has experienced only minor use for over 30 years. It is very insoluble in water and most organic solvents and, thus, extremely difficult to formulate. An oilborne formulation uses relatively expensive nickel-2-ethylhexoate as a co-solvent. A waterborne form is made with dodecylbenzene sulfonic acid, but the solution is highly corrosive to metals. Cu-8 is currently the only biocide listed in the AWPA Standards for treating wood that comes in contact with foodstuffs, and it continues to have the only CFR (Code of Federal Regulation) citation for use on wood with incidental food contact like bins for fruit and vegetables. A small volume of Cu-8 is used in the U.S. for above-ground applications and for sapstain and mold control, and minor amounts are sold as a brush-on preservative. Concerns have been raised about possible long-term health effects of the nickel carrier, and non-nickel oilborne formulations are now available. Recent developments in Cu-8 formulation with phosphate [or phosphite] ions show excellent progress toward the development of a waterborne preservative for pressure-treating residential lumber, and research in New Zealand has shown phosphate-formulated Cu-8 is suitable for many ground-contact and above-ground applications. Research is also being conducted on the *mono* form of Cu-8, which so far appears to have good efficacy in ground-contact studies against decay fungi and termites and may be easier to formulate in an oilborne or waterborne system than *bis* Cu-8.

Copper naphthenate is an organometallic biocide made by complexing copper with naphthenic acids. Copper naphthenate is relatively low cost and has been used for over 100 years for various applications in North America, including treating wood during WWII. It has low mammalian toxicity, broad activity against decay fungi and insects, is readily soluble in hydrocarbons, and has good stability and leach resistance. Since the 1990's some utility poles have been treated with oilborne copper naphthenate in North America, and it is being considered for other applications in states that have, or are considering, restricting creosote. Another commercial product used in several countries is the combination of copper naphthenate, borate, water and a thickening agent, with the mixture applied as a remedial ground treatment to utility poles followed by a tarpaper or plastic wrap. Fairly large amounts (2×10^6 kilograms) of copper naphthenate are also sold over-the-counter in both solvent-based and waterborne forms for applications such as brushing on cut surfaces of pressure-treated refractory lumber. Copper naphthenate imparts a green color to wood; for applications where no color is desired the slightly less effective zinc naphthenate can be used. A waterborne copper napthenate system is available in North America for non-pressure applications and which may soon be standardized for pressure treating applications.

Copper naphthenate has approximately 3% of the treated wood pole market in the U.S. and essentially all of the non-pressure fence post market.

Tributyltin oxide (TBTO) is an organometallic biocide which exhibits good activity against fungi and insects, is soluble in most hydrocarbons, and has good leach resistance. It is used as an above-ground solventborne or oilborne treatment for millwork and related applications in many countries. However, it undergoes slow dealkylation under certain conditions that reduces its fungicidal properties. Consequently, TBTO is most applicable for relatively low decay hazard areas and applications, such as millwork in Europe. Only four U.S. millwork (joinery) plants currently utilize TBTO.

A minor fixed-copper waterborne system is copper citrate (ammoniacal copper citrate, CC), which is effective in above-ground applications but weak against copper-tolerant fungi in ground-contact applications and susceptible to copper leaching. Only small amounts of CC-treated lumber are available in North America, and the original sponsors have requested that CC be withdrawn [no longer listed] from the AWPA Standards. Another complexed copper system is copper bis(dimethyldithiocarbamate) (CDDC), formulated with copper, ethanolamine and sodium dimethyldithiocarbamate (SDDC). Since copper reacts rapidly with SDDC to form an insoluble complex, a two-step water-based treating process is required. This gives a stable, noncorrosive and nonleachable preservative with good activity against most wood-destroying organisms but the dual treatment increases the cost. CDDC is no longer listed by the AWPA and is not commercially available.

3. Organic Biocides/Preservatives

3.1 Commercial Organic Biocides/Preservatives

The "new" waterborne copper-rich systems, including ACQ, CA, and Cu-HDO/CX, used to pressure-treat lumber in North America, Europe, and/or Asia do not contain arsenic or chromium. However, as mentioned above these systems also have some disadvantages. For example, they contain relatively high levels of copper and metallic-treated wood may face future disposal problems. Disposal is already a concern in Europe and Asia, and Denmark and Norway have greatly limited copper-containing preservatives. Thus, organic-based systems are being developed. While wood treated with organic systems may be easier to dispose of in the future, totally-organic systems also have some concerns. Among these is formulation; most organics are water insoluble but U.S. residential preservative systems will likely be waterborne. This is due to the low cost, safe and non flammable properties of water, the lack of organic vapor emissions and odors, and the clean and non-oily surface which is obtained when lumber is treated with a waterborne system. Another concern with organic systems is biocide depletion; while the cause of copper depletion is water-related leaching, organic bioicides can also undergo biological, photo/sunlight and chemical degradation, and possibly evaporation. Additionally, most new organic biocides do not have the broad efficacy against the numerous wood destroying organisms that the older biocides have. Thus, many organic wood preservatives combine two or three biocides to obtain broad protection. Finally, while some organic systems are already available in Europe and perform well in above-ground applications in areas with low decay hazard, developing an economical and effective organic system for ground-contact residential applications in high degradation hazard areas, such as the southeastern U.S., will be relatively difficult. At the present time no totally-organic, water-based system for exterior residential applications has been standardized by a U.S. regulatory agency, although a proposal for an organic above-ground residential system has just been submitted to a U.S. standard-setting organization.

The azoles, or more properly triazoles, include cyproconazole, propiconazole and tebuconazole. They are extremely active against wood decaying fungi, readily soluble in hydrocarbon solvents and exhibit good stability and leach resistance in wood. Although azoles are expensive, their high activity allows use of very low levels which makes them relatively cost effective. Disadvantages include no activity against sapstains, molds and insects/termites. Thus, azoles are usually combined with other fungicides and/or termiticides. Waterborne copper azoles (CA), discussed above, are one of the main preservatives in the U.S. and elsewhere, and other commercial preservatives in Europe based on an azole combined with another biocide are discussed below. Current research in the U.S. is examining above-ground samples treated with propiconazole and/or tebuconazole, and a proposal has just been submitted to a U.S. standard-setting organization for an above-ground preservative system which consists of these two azoles and the insecticide imidacloprid.

3-Iodo-2-propynylbutyl carbamate (IPBC, Polyphase™) is an organic biocide with low mammalian toxicity. It is readily soluble in hydrocarbon solvents, and has a broad range of activity against decay and mold fungi. However, IPBC has no insect activity and its long term effectiveness is questionable. As a sole biocide, solventborne IPBC in North America is currently used for millwork-type applications, and until recently IPBC was combined with the insecticide chlorpyrifos as an oilborne treatment for above-ground beams, etc. IPBC was examined as a co-biocide in other wood preservative systems, but U.S. interest has declined. In Europe many combinations of IPBC and propiconazole, or IPBC, propiconazole and tebuconazole, solventborne or waterborne, are used in above-ground applications. IPBC is the active ingredient in many brush-on preservatives sold over-the-counter in North America, and the combination of IPBC and DDAC is used for sapstain and mold control. Almost all of the millwork (joinery) wood preservative systems in North America utilize IPBC as an active ingredient in their wood treatment system.

Several types of quaternary ammonium compounds (quats) are available. These include didecyldimethylammonium chloride (DDAC, Bardac 22™) and other similar dialkydimethylammonium chlorides with C_8-C_{14} alkyls, and the alkyldimethylbenzyl ammonium chlorides (alkyl benzyldimethylammonium chlorides, benzalkonium chlorides, BAC's, ABACs, ADBACs), usually sold as a mixture with C_{12} - C_{18} alkyl groups. To reduce corrosion, some quats are available with the chlorine anion replaced with other anions such as carbonates. The quats have very low mammalian toxicity, are relatively inexpensive, have broad activity against decay fungi and insects, are soluble in both water and hydrocarbon solvents, and exhibit excellent stability and leach resistance due to ion-exchange fixation reactions with wood. However, their efficacy is only moderate and when quats are used alone the wood may not be adequately protected. Another disadvantage is that quats, as surfactants, make wood exposed to rain pick up moisture more easily. Due to their surfactant properties and low cost quats are often combined with other biocides. For example, copper and quats are the active ingredients in waterborne ACQ*,* discussed above, and DDAC plus IPBC is a commercial sapstain and mold agent. Quats will undoubtedly continue to be considered in new preservative systems. In addition, some quat precursors such as tertiary amines are increasingly used in the U.S. as corrosion inhibitors and anti-fungal surfactants in sapstain formulations.

Polymeric betaine (didecyl-bis(2-hydroxyethyl ammonium borate, didecylpolyoxethylammonium borate, betaine), is an oligomer based on alternating quat and borate ether units. Both the quat and borate groups can bind to wood to make the borate relatively less susceptible to leaching. Polymeric betaine is active against both decay fungi and insects. Waterborne systems commercially available in Europe include polymeric betaine alone or combined with an organic insecticide for above-ground applications and with uncomplexed copper for ground-contact applications. Research studies on polymeric betaine systems are underway in the U.S.

The synthetic pyrethroids (Permethrin, Bifenthrin, Cypermethrin, Cyfluthrin, and Deltamethrin, with others being developed), analogues of natural terpenoid pyrethrins, have low mammalian toxicity, exhibit good efficacy against insects but are not fungicidal. They are soluble in many hydrocarbon solvents. In the U.S. research on the combination of a synthetic pyrethroid and fungicide has been conducted, and permethrin is sold over-the-counter for termite control. In Europe several combinations of a synthetic pyrethroid and other biocide(s) are available, including a quat combined with permethrin and tebuconazole, or a cypermethrin and tebuconazole mixture to protect wood, and permethrin is used to protect plywood against insects.

3.2 *Organic Agrochemcials with the Potential to Protect Wood*

In the past two decades many agrochemicals have been evaluated as potential wood preservatives. Most of these are already registered and labeled for non-wood agricultural applications. Examining registered agrochemicals for their potential to protect wood has the advantage that the cost of label expansion is less than the cost required to develop, test, then register and label an entirely new biocide for the relatively small wood preservation market. Compounds listed below are organic agrochemicals which, based on prior or on-going studies, may have potential as wood preservatives.

Busan 30™ (2-(thiocyanomethylthio) benzothiazole, TCMTB) is an organic biocide with a broad range of activity against both fungi and insects, is readily soluble in hydrocarbons and exhibits good leach resistance in wood, but it is susceptible to biodegradation. It has broad spectrum use as an anti-mold and anti-sapstain biocide, and minor use in the protection of joinery/millwork.

Chlorothalonil (2,4,5,6-tetrachloroisophthalonitrile, TCPN, CTL) is an organic biocide with very low mammalian toxicity, broad activity against decay fungi and insects, relatively low cost, and good leach resistance in wood. A major research effort in the 1990's examined chlorothalonil as an alternative for penta. However, the poor solubility of chlorothalonil in most organic solvents made formulation difficult and interest in pressure treating applications has waned. Chlorothalonil, alone or combined with methylene bis-thiocyanate (MBT), is used in many anti-sapstain and anti-mold systems in North America,

Dichlofluanid (1,1-dichloro-N-[(dimethylamino)sulfonyl]–1-fluoro-N-phenyl-methanesulfenamide, DCFN) is a fungicide used in paints and stains in Europe. DCFN may have potential as a fungicide for lumber and wood composites.

Fipronil (5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethyl)sulfinyl]-1H-pyrazole-3-carbonitrile) is an insecticide which, when combined with a fungicide, has been examined as a wood preservative.

Imidacloprid (1-[(6-chloro-3-pyridinyl)methyl]-N-nitro-2-imidazolidinimine, Preventol™) is a neo-nicotinoid insecticide. Field tests in the U.S. showed that imidacloprid had much greater efficacy than chlorpyrifos in protecting wood against termite attack, and studies have shown good long-term stability and leach resistance. Imidacloprid is a component of a totally organic system which has just been proposed for U.S. above-ground applications.

The isothiazolone 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (Kathon 930™) is a biocide with moderately low mammalian toxicity, broad activity against decay fungi and termites, is readily soluble in hydrocarbons, and exhibits excellent stability and leach resistance in wood. Research has shown that Kathon 930™ effectively protects wood in both ground-contact and above-ground applications, but no commercial formulations are currently available for wood. Other isothiazolone analogues are used in many different products, including short-term control of molds and sapstains on wet, freshly-treated lumber.

Methylene bis-thiocyanate (MBT) is a sulfur-based biocide with a broad range of efficacy against many decay, mold and sapstain organisms. No data has been reported on its efficacy against insects. In the U.S. it is commonly combined with other biocides and insecticides. MBT has large scale use in the paper industry as an effective algaecide in non-alkaline systems.

Oligomeric alkylphenol polysulfide (PXTS) is an oligomer consisting of a mixture of alkylphenols linked by 2-10 sulfurs, with a low degree of polymerization. This biocide has many of the same characteristics and efficacy as creosote in marine and ground-contact tests currently underway. PXTS has a very low mammalian toxicity profile (Oral $LD_{50} > 5g/kg$) and is environmentally benign. The AWPA has just standardized PXTS as a wood preservative in above-ground applications and other applications are being considered, but this system is not currently commercially available.

4. **Formulation of Biocide(s) into a Commercial Wood Preservative**

Once a biocide, or a combination of biocides, has been selected it is formulated into a commercially useful system. For treating solid wood products (lumber, poles, etc.) and many wood composites, the biocide is typically dissolved in a carrier to give a liquid preservative system. Thus, an important consideration is the choice of carrier. For industrial applications either an oilborne or waterborne system can be used. Heavy oil carriers by themselves provide some protection against decay fungi and termites, and the oily surface and petroleum odor is usually not a problem for industrial applications. For residential applications a light petroleum carrier is possible but problematic; all current North American residential pressure-treating systems are waterborne for reasons discussed above (some over-the-counter preservatives for brush-on application by the homeowner are solventborne). However, since most of the newer organic agrochemicals are highly insoluble in water, an oil-in-water emulsion that is commercially robust will need to be developed.

Other considerations, especially for residential applications, in the development of wood preservative formulations include: able to be concentrated for ease of shipment; safe to use at the treating plant with the treated wood harmless to consumers; have good penetration into solid wood during the treating process; exhibit little depletion and have good long-term stability; have little or no odor and leave the lumber with an attractive and paintable surface; are non-corrosive to metal fasteners; have no significant effect on wood strength; and results in a treated wood product that can be safely and easily disposed of at end of product life.

Once a formulation has been developed and all components and systems approved by the many regulatory agencies, it can be used to treat wood. The vast majority of wood products are treated by a vacuum/pressure process. Products treated by this method are called pressure-treated, and include treated lumber and plywood sold at hardware stores, utility poles, marine pilings, railroad ties, etc. The pressure treating process gives the uniform biocide retentions and deep penetration necessary to ensure long-term performance. In this process the wood is usually first dried then placed in a pressure-treating cylinder, a vacuum is drawn and the preservative solution added to the cylinder. Pressure is then applied to force the solution deep into the porous wood; a vacuum may be drawn in the final process step. The treated wood product is then subjected to rigorous quality control analysis to ensure that the product meets published specifications. Over-the-counter preservatives are generally brushed on by homeowners and only provide short-term protection. Control of sapstain and mold on wet lumber is accomplished by dipping or spraying, and window frames, farm fence posts, etc. are treated by dipping, soaking or spraying.

An alternative to a liquid pressure-treating system includes a supercritical fluid process, but this requires very high capital costs. Vapor-phase treatment with trimethyl boron has also been studied. Some biocides are added directly, as a powder or liquid, to the wood furnish [wood particles, flakes, veneers, etc.] during the manufacture of composites such as oriented strandboard or particleboard. Typical biocides added during composite manufacturing are zinc borate or copper. Alternatively, the same liquid preservatives used to treat lumber and poles can be used to pressure treat some manufactured wood composites such as plywood, and laminated beams can be made from already-treated lumber.

5. **Non-Biocidal Alternatives to Biocide-Treated Wood**

The heartwood [dark colored center in mature logs] of certain trees is naturally resistant to decay fungi and/or termites. Naturally-durable U.S. lumber includes redwood, western red cedar, and cypress. This lumber is relatively expensive and harvest restrictions may limit future availability. Other potential problems are that the sapwood [the light-colored recent growth in the outer portion of a mature log] is not durable but may be stained to match the color of the heartwood. Also, since the heartwood is durable due to toxic extractives, contact with naturally durable lumber or sawdust may cause skin irritation or other health problems.

It has long been known that heating lumber in a non-oxidative environment will enhance the decay resistance of wood and improve dimensional stability, but this treatment significantly reduces the strength properties and the lumber is not resistant to insects. Commercial production of heat-treated lumber is growing rapidly in Europe and the wood appears suitable for non-structural, above-ground applications in low decay hazard areas.

Addition of a water repellent to lumber for above-ground applications lowers the amount of moisture gained during rainstorms and, consequently, lowers the decay potential. Water repellents also increase the dimensional stability of lumber and, if a biocide is present, the depletion potential is reduced. Most water repellents are wax- or oil-based and, thus, cost-effective and safe. Lumber co-treated with the ACQ or CA systems and a water repellent are available in North America as premium-grade decking. Lumber treated with linseed-oil based water repellent is being studied in Europe, but mold is a problem. Treating wood with high levels of wax is being examined in the U.S., but high summer temperatures can lead to unsightly bleeding/oozing. Over-the-counter water repellents sold to U.S. homeowners for brush-on applications are usually formulated with wax, or wax plus aluminum stearate, and a biocide such as IPBC might also be present. Brush-on systems only provide short-term protection, however.

Fungi degrade wood by free-radicals that are generated via metal-mediated chemical reactions. Both free radical scavengers (antioxidants) and metal chelators are commercially available and, as many are approved food additives by the U.S. Food and Drug Administration (FDA), often benign. Several laboratory studies have found that combining antioxidants and/or metal chelators with various organic biocides greatly enhances biocide efficacy, often by two- or three-fold. Outdoor above-ground or ground-contact samples treated with combinations of organic biocide/antioxidant/metal chelator/water repellent show promising results so far. Most of these studies have used the antioxidant BHT, which is low cost, nonleachable and benign [BHT has a GRAS (Generally Recognized As Safe) classification by the U.S. FDA, which allows it to be directly added to human foodstuffs]. Preliminary results suggest that an antioxidant may also help protect organic biocides against microbial degradation.

Other possible non-biocidal methods to protect wood include modification of the chemical groups in wood, and resin impregnation of lumber. However, these treatments are relatively expensive and process control may be difficult. The most promising chemical modification process appears to be acetylation. This process was first proposed about 40 years ago and has recently had renewed interest. If sufficient hydroxyl groups are acetylated the wood has good decay and termite resistance and is dimensionally stable. However, acetylated lumber may have even greater metal corrosion problems than lumber treated with CA or ACQ. There is also some interest in furfurylated wood in Europe. Treatment of lumber with low cost sodium silicate, sometimes with a co-added water repellent, is also being proposed for protecting lumber against termites. The silicate apparently acts as a gritty material and physically hinders termites. The use of microorganisms that are antagonistic to wood-degrading fungi or insects has been studied and some limited marketing occurred for a brief time in Europe, but there were concerns over long-term effectiveness and this approach is apparently no longer commercial in Europe. This biocontrol concept may be most applicable for short-term control of molds and stains on wet lumber.

6.0 Trends in Wood Preservation

Due to environmental considerations, public concerns over bioactive chemicals and governmental regulations, wood preservation has undergone dramatic and profound changes on a world-wide basis in the past 15 years, especially for residential applications. In the U.S. CCA-treated lumber for most residential applications has been replaced by the slightly more expensive lumber treated with the copper-rich CA and ACQ systems. Misuse and/or poor construction practices, such as not using stainless-steel or hot-dipped galvanized fasteners or joist hangers, may lead to early failures and consumer distrust which will increase the use of alternatives to solid lumber.

The waterborne 2nd generation copper-rich systems for exterior residential applications in North America are ACQ and CA. These, plus the Cu-HDO/CX, CCB, and Cu-polymeric betaine systems available in Europe and/or Asia, have mostly replaced CCA. However, these systems have their own concerns, such as the ultimate disposal of metal-treated lumber. Indeed, several European countries are already requiring total-organic systems for most applications. In the U.S., the 1st generation CCA, penta and creosote systems may continue to be approved for industrial applications, but totally-organic, or low-metallic systems such as copper naphthenate or Cu-8, may be required for residential applications at some future point. Developing effective and economical totally-organic systems, especially for ground-contact applications in high deterioration hazard areas such as the southeastern U.S., may prove challenging and the cost of treated wood will undoubtedly increase.

One problem with developing an organic system for preserving wood is that the total market for wood preservative biocides is relatively small, about US$ 540 million in direct sales world-wide, with two-thirds of that in North America. This market is very small compared to the tens of $ billions market for agrochemicals, making it difficult for a company to justify spending the considerable resources necessary to develop, test, and label a new biocide. Thus, most of the new organic biocides being examined for wood protection are already labeled for agrochemical applications and commercially available. However, the desired properties for a wood protection chemical differ greatly from that for an agrochemical. For example, agrochemicals are typically applied to a crop to control a specific pest for only a few weeks. In contrast, preservatives are expected to protect wood against a wide variety of fungi and insects for many years. Also, the value of the biocide used to protect wood is a relatively small fraction of the total value of the product, but if the treated product fails the biocide company is liable for the entire amount; i.e., the chemicals used in wood protection has a small market value but carries a high liability potential.

The 1st generation systems were extremely forgiving in the treating process and in use. For example, wood is extremely variable and, consequently, the individual boards in a load of lumber treated together with CCA have a wide range of biocide retentions. CCA was so effective, however, that all the lumber usually performed satisfactory. The high cost of the newer organic biocides and the need to keep the cost down has led to wood preservative proposals with relatively low biocide retentions being submitted to regulatory agencies. While the proposed biocide retention may have performed satisfactory with the small stakes used in research studies, commercial-size lumber generally has greater within- and among-retention variability. The result is that some fraction of the lumber in one load may be undertreated with the potential for early failure. The high efficacy of some of the newer biocides has resulted in very low retention levels being considered, so the macro- and micro-biocide distribution in wood may become important. Also, metals can only be depleted by leaching. However, the newer organic biocides not only leach but are degraded by various microorganisms, and loss can also occur due to chemical and photo/sunlight reactions and possibly volatilization. Furthermore, some suppliers are submitting proposals of new systems to building code-writing agencies which may not be familiar with treated wood and, consequently, may not recognize systems that have not been subjected to rigorous, comprehensive and long-term testing. Also, inappropriate use of treated wood, such as constructing an exposed deck using borate-treated (SBX) lumber, could happen with someone not familiar with the new preservative systems. Finally, many of the newer systems have been found to be more sensitive to the treating process than the relatively forgiving older systems. Thus, certain treating or handling practices that were common in the past may cause problems with the newer systems. Unless properly addressed some or all of these above items have caused, or will cause in the near future, treated wood products to fail. The inevitable result will be an accelerated demand for non-wood materials in residential applications.

Two examples of newer systems which recently experienced some failures and subsequent legal liability are copper naphthenate and TBTO. When copper naphthenate-treated poles were first introduced in the 1990's a few of the southern pine poles experienced severe and early decay, some as soon as two years after installation. The lack of performance was totally unexpected since extensive long-term outdoor ground-contact tests conducted at a number of locations showed good performance for stakes treated at the recommended level. Furthermore, most of the southern pine poles, and all of the Douglas-fir poles, performed satisfactorily, and analysis of the failed poles showed that the copper retention was in the approved range. The reason for the early failure of these copper naphthenate-treated poles has not been fully determined, but it appears that handling of the treating solution, poor treating practices and an analytical procedure which only measured the copper metal content [as opposed to determining the level of copper naphthenate] may have been factors. Procedures that only determine the metal content of complexed metal biocides may have also contributed to problems associated with TBTO-treated window frames. Specifically, after some years of service poor performance of TBTO-treated wood was observed. Eventually it was determined that TBTO was susceptible to slow de-alkylation to form dibutyl and monobutyl compounds, with the recommended tin content present but the dealkylated organometallic having considerably less fungicidal activity.

Another problem in developing wood preservative systems is the wide variety of deterioration conditions, wood-destroying organisms, and soils [physical and chemical properties of soil not only affect microorganism type and quantity present but also impact decay and leaching potential] in different parts of the U.S. In addition, while research is underway to develop faster laboratory tests to evaluate the efficacy of new preservatives, experience has shown that unless significantly more progress in laboratory test methodology is made it is best to subject treated wood to a wide variety of outdoor exposure sites for many years to fully evaluate a preservative. The high liability potential, discussed above, also generally causes suppliers to subject potential preservatives to exhaustive and lengthy tests. However, changes in wood preservation in North America, brought about by governmental regulations or a voluntary withdrawal by the suppliers, have occurred very rapidly. Also, future totally-organic systems will be much more complex than the 1st generation systems. Specifically, older wood preservatives were generally based on only one biocide that had broad efficacy against a wide variety of wood-destroying organisms, but future systems will likely be composed of two or more biocides with other non-biocidal additives possibly added. Complete and meticulously testing of these multi-component mixtures will be difficult, especially given likely time constraints. Finally, public perceptions and concerns about bioactive chemicals, whether based on good science or not, are frequently a major factor in determining governmental policy and public acceptability.

7.0 Conclusions

Extensive and costly biodegradation occurs to untreated wood exposed to the weather or in ground contact, or unexposed wood in areas with high potential for termite attack. A portion of this damage can be avoided by better residential design and/or construction techniques, and lumber treated with the relatively benign borates can be used in limited, non-exposed conditions. However, wood products treated with biocides will still be necessary in the U.S., especially for exposed residential use in moderate to severe hazard areas and industrial applications. Prior to January 2004, CCA was used to treat most preserved lumber in North America. Currently, for most residential applications CCA has been replaced by the water-borne copper-rich ACQ and CA systems and, to a very limited extent, by the waterborne borates. The two copper-rich systems are about as effective as CCA when correctly used. The disadvantages of the newer systems include higher costs, much greater potential for metal corrosion, increased copper leaching and more apparent mold growth on freshly-treated wet lumber.

The replacement of CCA with the newer wood preservatives for most residential applications has occurred in an extremely short period in North America. Inappropriate treatment, use and/or construction practices may occur with the result that some wood products treated with the newer systems may perform unsatisfactorily. This can be minimized by careful attention to proper treating practices and aggressive consumer education, but some problems will undoubtedly occur which will accelerate demand for non-wood construction materials. Further changes in wood preservative systems for residential applications may occur at some future point, due to environmental and/or government regulations. One possibility may be the requirement for totally-organic residential systems; this is already occurring in some European countries. The development of effective and economical totally-organic residential ground-contact systems, especially in areas of the U.S. with high or severe deterioration conditions, will prove challenging. Consequently, in the near term wood protection companies may face many challenges. However, if chemical and/or processing systems can be developed which provide wood products with dependable and desirable properties and allow companies to obtain a fair profit for the research and testing activities required to develop these innovative wood-based materials, then the wood protection industry may prosper in the long run.

8. Authors' Note

The mention of trade names is for the convenience of the readers and is not intended to constitute endorsement of a particular product over other equally suitable products. This article was written in the summer of 2004. Due to the rapid changes in wood preservation, the status of some systems may have since changed and some new systems/biocides may be available.

9. Further Reading

American Wood-Preservers' Association Standards 2002. Granbury, Texas, U.S. [Lists all biocides, and preservatives, currently standardized by the AWPA.]

American Wood-Preservers' Association Proceedings 2003. Selma, Alabama, U.S. [The latest updates are presented on CA, ACQ, borates, CCA, creosote, CX, penta, and waterborne and oilborne copper naphthenate systems.]

Barnes, H. M., Murphy, R. J. (1995). "Wood Preservation: The Classics and the New Age." *Forest Products Journal*, 45(9), pp 16-26.

Barnes, H. M. (2001). "Wood: Preservative Treated." *Encyclopedia of Materials: Science and Technology*. Elsevier Science Ltd., London.

Eaton, R. A., Hale, M. D. C. (1993). *Wood: Decay, Pests and Protection.* Chapman & Hall, London.

Edlund, M.-E., Jermer, J. (2002). Evaluation of Wood Preservatives for Nordic Wood Preservation Class AB. *The International Research Group on Wood Preservation*, Paper IRG/WP 02-30297.

Evans, P. (2003) "Emerging Technologies in Wood Protection." *Forest Products Journal,* 53(1), pp 14-22.

Freeman, M. H., Shupe, T. F., Vlosky, R. P., Barnes, H. M. (2003) "Past, Present, and Future of the Wood Preservation Industry." *Forest Products Journal* 53(10), pp 8-15.

Goodell, B., Nicholas, D. D., and Schultz, T. P. (2003). *Wood Deterioration and Preservation: Advances in our Changing World*. American Chemical Society, ACS Symposium Series 845, Washington, DC.

Morrell, J. J., Morris, P. I. (2002). Methods for Improving Preservative Penetration into Wood: A Review. *The International Research Group on Wood Preservation*, Paper IRG/WP 02-40227.

Nicholas, D. D. (2001). "The Preservation of Wood." Hon, D. N.-S., Shiraishi, N. (eds.) *Wood and Cellulosic Chemistry, 2nd edit.* pp. 795-806. Marcel Dekker, Inc., New York.

Preston, A. F. (2000). "Wood Preservation: Trends of Today That Will Influence the Industry Tomorrow." *Forest Products Journal* 50(9):12-19.

Rapp, A. O., ed. (2001). Review of Heat Treatments of Wood. *European Commission, COST Action E22, Report EUR 19885*, Rue de la Loi, Brussels.

Reich, M. S. (2004). "All Hands on Deck." *Chemical and Engineering News* 82(32):14-16.

Schultz, T.P., Nicholas, D.D., Dalton, T.J., Keefe, D. (2004). "Biocide Retention Variation of Southern Yellow Pine Products Treated with Waterborne Preservatives in Commercial, Pilot Plant, or Laboratory Cylinders." *Forest Products Journal* 54(3):85-90.

Schultz, T.P., Nicholas, D.D. (2004). "Protection of Wood Against Biodeterioration". Evan, J., Youngquist, J.A. (eds.) *Encyclopedia of Forest Sciences; Solid Wood Processing*, pp. 1274-1282. Elsevier, Oxford, U.K.

Suttie, E. D., Bravery, A. F., Dearling, T. B. (2002). Alternatives to CCA for Ground Contact Protection of Timber: A Perspective from UK on Performance and Service Life Expectations. *The International Research Group on Wood Preservation*, Paper IRG/WP 02-30289.

Wilkinson, J. G. (1979). *Industrial Timber Preservation*. Associated Business Press, London.

Zabel, R. A., Morrell, J. J. (1992). *Wood Microbiology: Decay and Its Prevention*. Academic Press, New York.