time, and then another vacuum step to remove excess anhydride is used. Microwave energy is then applied to heat the anhydride soaked wood.

The penetration depth of the microwaves at 2450 MHz is approximately 10 cm, which means this technology can be used to acetylate large wood members. The variation in acetyl content, both within and between samples, is less than 2%. Microwave energy can also be used to remove the excess acetic anhydride and by-product acetic acid after acetylation.

One of the concerns about the acetylation of lignocellulosics, using acetic anhydride as the reagent, has been the by-product acetic acid. Many attempts have been made for the 'complete removal' of the acid to eliminate the smell, make the process more cost effective, and to remove a chemical potentially causing ester hydrolysis. Complete removal of by-product acetic acid has now been achieved in both the fiber process and the solid wood microwave process.

*See also*: **Solid Wood Processing**: Adhesion and Adhesives; Finishing; Protection of Wood against Biodeterioration; Wood-based Composites and Panel Products. **Wood Formation and Properties**: Chemical Properties of Wood; Formation and Structure of Wood.

## Further Reading

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# Protection of Wood against Biodeterioration

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## Introduction

Wood and wood composites are degraded by many organisms, including brown, white and soft rot fungi, termites and other insects, bacteria, and marine borers. Traditionally, the wood protection industry has relied on a few preservatives which have a broad range of activity, with cost and efficacy being the major considerations. However, governmental regulations, public perceptions, and environmental and disposal issues have resulted in rapid and profound changes. Further compounding the difficulty for industry is the relatively low market value for wood-preserving biocides, about US$200 million in direct sales annually worldwide in 2000, two-thirds of that in North America. Other problems are that the cost of the biocide is only a small fraction of the total value of the treated wood product, but biocide failure will entail replacement of the entire product (i.e., the biocide has a relatively low value but carries a high liability potential), and the long service life expected of treated wood products.

## Biocides

Wood can be colonized and degraded by a variety of organisms. In addition, a preservative must be effective for many years during which the biocide level can be reduced by leaching, evaporation, and/or degradation. Thus, biocides for preservatives must be thoroughly tested by lengthy outdoor exposure. Even after years of testing and commercial use, unforeseen problems may arise. Also important is the biocide level required to protect wood adequately for a particular application and location. Warm and moist climates generally have greater decay and/or insect hazard than cool and/or dry locations and, thus, require higher biocide levels. Generally, biocide levels vary for different applications such as above-ground, ground-contact/residential, ground-contact/industrial, and marine exposure. For example, retentions for chromated copper arsenate (CCA) treated southern pine wood in the United States are 4.0, 6.4, 9.6 or 12.8, and 24 or 40 kg $m^{-3}$ for the above applications, respectively.

All biocides must be registered with the appropriate governmental agency which ensures that all products are safe; in the United States the agency is the Environmental Protection Agency (EPA) under the Federal Insecticide, Fungicide and Rodenticide Act, with other possible additional requirements by individual state agencies. Other countries have similar agencies and requirements. Use of a registered bioactive compound still carries some inherent health risk, however. To register a compound, a company must conduct extensive testing on the toxicological and other health effects, environmental fate, etc. Once registered the company then develops a 'label' which, after acceptance by the appropriate regulatory agency, clearly lists the specific applications and quantifies the amounts for which the formulated biocide product can be legally used; use of a registered biocide for any nonlabeled application is not permitted. Additional nonlabeled applications for a registered compound can be proposed following further testing, termed supplemental labeling or label expansion.

The 'traditional' wood preservatives are creosote oil, oilborne pentachlorophenol (penta), and waterborne arsenicals. These three systems effectively and economically control many of the fungi, insects, and marine borers that attack wood. Arsenicals, principally CCA, currently are, or were, the major preservatives in many countries. For example, in 1997 CCA was used for about 80% of all wood treated in the United States. However, recent public concerns about arsenic have led to restrictions that will reduce CCA usage by about 70% in the United States as CCA is delabeled (no longer approved) for residential applications by 2004. Most European countries have already limited or totally banned CCA with further restrictions likely, and Japan has almost entirely converted to preservatives without arsenic or chromium. Use of alternative copper : organic systems is expanding, but these copper-rich second-generation systems may also be restricted in the future with totally organic preservatives mandated; this trend is already apparent in some European countries.

## Commercial Wood Preservatives

Biocides that are commercially used at this time to protect wood are discussed below and shown in **Table 1**, starting with the three traditional systems and then listing the 'newer' systems alphabetically, with potential biocides then discussed and shown in **Table 2**.

**Chromated copper arsenate/arsenicals** Of the arsenicals, CCA is unquestionably the principal wood preservative in many countries. CCA is very effective, economical, dependable, waterborne and leaves lumber with a clean and nonoily surface. Thus, CCA usage has greatly increased in the past 30 years, especially for residential applications. About 75 000 tonnes (oxide basis) was consumed in 2000 in North America and about 15 000 tonnes in Europe, but

**Table 2** Biocides with the potential to protect wood, pending further development

| *Common name* | *Chemical name* |
|---|---|
| Chlorothalonil | 2,4,5,6-Tetrachloroisophthalonitrile |
| CDDC | Copper(II) mono(dimethyldithiocarbamate) |
| Dichlofluanid, DCFN | 1,1-Dichloro-*N*-[(dimethylamino) sulfonyl]-1-fluoro-*N*-phenylmethanesulfenamide |
| Imidacloprid | 1-[(6-chloro-3-pyridinyl) methyl]-*N*-nitro-2-imidazolidinimine |
| Fipronil | 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethyl)sulfinyl]-1*H*-pyrazole-3-carbonitrile |
| Kathon 930™ | 4,5-Dichloro-2-n-octyl-4-isothiazolin-3-one |
| PXTS | Polymeric xylenol tetrasulfide |
| TCMTB, Busan 30™ | 2-(Thiocyanomethylthio) benzothiazole |

**Table 1** Biocides and biocide combinations used commercially as wood preservatives

| *Common name(s)* | *Chemical name* |
|---|---|
| Arsenicals (CCA)[a] | Chromated copper arsenate, CuO, $CrO_3$, $As_2O_5$ |
| Creosote | Creosote, Coal tar distillate |
| Penta, PCP | Pentachlorophenol |
| Azoles (Tebuconazole)[a] | (3*RS*)-5-(4-chlorophenyl)-2, 2-dimethylethyl-3-1*H*-[1,2,4-triazole)methyl]-3-pentanol |
| Borates, Timbor™, DOT | Disodium octaborate tetrahydrate |
| Copper/chromium systems (CCB)[a] | Chromated copper borate, $CrO_3$, CuO, $B(OH)_3$ |
| Copper azole, CA, CBA | Copper(II) + tebuconazole + [boron] |
| Cu-HDO | Copper(II) bis-*N*-cyclohexyldiazeniumdioxy + CuO + boric acid |
| Copper citrate, CC | Ammoniacal copper(II) citrate |
| Copper quats, ACQ | Alkaline copper(II) quats, CuO + quats |
| Oxine copper, copper-8 | (bis)Copper-8-quinolinolate |
| Copper naphthenate | Copper(II) naphthenate |
| IPBC, Polyphase™ | 3-Iodo-2-propynlbutyl carbamate |
| Quats (DDAC)[a] | Quaternary ammonium compounds (didecyldimethylammonium chloride) |
| Synthetic pyrethroids (Permethrin)[a] | Cyclopropanecarboxylic acid, 3-(2,2- dichloroethenyl)-2, 2-dimethyl-(3-phenoxyphenyl) methyl ester |
| TBTO | Tributyltin oxide |
| Zinc borate | Boric acid + zinc salt, 2 : 3 |

[a] A class of compounds, of which several individual compounds are used to protect wood. An example of one compound is shown.

usage will shortly be dramatically lower. Formulations with different ratios of chromium, copper, and arsenic are available; in the United States CCA-type C is used which contains 18.5% copper (as CuO), 47.5% chromium (as $CrO_3$), and 34.0% arsenic (as $As_2O_5$). CCA is effective against a wide variety of wood-consuming fungi, insects, and marine borers, but ineffective against the small fraction of insects, marine borers, and stain/mold fungi that inhabit but do not consume wood as a food source. Waterborne, CCA becomes fixed by a complex series of redox, complexing and precipitation reactions with wood and, once fixed, resists leaching. CCA-treated softwoods perform extremely well, but CCA-treated hardwoods can sometimes fail due to poor microdistribution. Another arsenical preservative is ammoniacal copper zinc arsenate (ACZA). ACZA is limited to treating refractory (difficult to treat) species, such as those present in western North America where the alkaline solution provides better penetration, but it is not as highly fixed as CCA.

**Creosote** Creosote is a preservative oil that has been used for more than 150 years. It is a coal tar distillation product, and is mainly composed of a complex mixture of polyaromatic hydrocarbons. It is sometimes combined with coal tar, especially for marine systems. Creosote is a thick black tar which is generally heated prior to impregnation into the wood. It is effective against a variety of wood-colonizing organisms and used to treat railroad ties, utility poles, and pilings, accounting for about 10% of the treated wood volume in North America. Recent concerns over possible mutagenic properties have reduced usage in some countries. A pigmented and emulsified formulation (PEC) is available in Australia, but treatment problems have arisen and interest has waned. An emulsion system is being examined in Europe.

**Pentachlorophenol** Pentachlorophenol (penta, PCP) is effective against a variety of wood-destroying organisms and stain and mold fungi, is inexpensive and readily soluble in hydrocarbons. Thus, penta has replaced creosote in many industrial applications. However, due to environmental concerns many countries have reduced or banned penta. It is currently used in about 10% of all treated wood in North America, primarily for utility poles. It can be formulated with a variety of heavy or light organic solvents, and salt and emulsion water-based systems are also possible. Poor performance can occur with some light solvent, emulsion, and salt-based systems because of inadequate distribution and/or leaching.

**Azoles** The azoles, or more properly triazoles, include cyproconazole (1*H*-1,2,4-triazole-1-ethanol, α-(4-chlorophenyl)-α-(1-cyclopropylethyl)), propiconazole ((2*RS*, 4*RS*)-2-(2,4-dichlorophenyl)-2-[1-1*H*-(1,2,4-triazole)methyl]-4-propyl-1,3-diaxolane), and tebuconazole ((3*RS*)-5-(4-chlorophenyl)-2,2-dimethylethyl-3-(1*H*-[1,2,4-triazole]methyl)-3-pentanol). They are highly 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 makes them relatively cost effective. Disadvantages include minimal or no activity against sapstains, molds, and insects/termites. Thus, azoles are usually combined with other fungicides and/or termiticides. Copper azoles (CA), and other commercial preservatives in Europe based on an azole combined with another biocide, are discussed below.

**Borates** Borates (borax, boric acid, disodium octaborate tetrahydrate (DOT), sodium borate) are inorganic boron-based biocides, generally formulated as a mixture of borax and boric acid. Borates have extremely low toxicity to mammals and a broad range of activity against decay fungi and insects, and are inexpensive and readily soluble in water. However, water solubility limits applications to those with minimal or no leaching exposure. Borates are used as a sole biocide in many countries. Borates are also a component in some newer nonarsenical copper : organic systems, but the boron is highly susceptible to leaching. Borates are also used as a diffusible biocide for the remedial treatment of millwork and related applications in many countries. Studies examined treating wood by a vapor process with trimethyl borate, which then reacts with the residual water in lumber to form boric acid. Several groups have examined compounds which form complexes with borates, or the use of water repellents, to reduce leaching.

**Copper/chromium systems** Chromated copper borate (CCB) and related copper/chromium systems are used in Europe, but environmental concerns may limit future applications of these systems. In the United States acid copper chromate (ACC) is listed in the American Wood-Preservers' Association (AWPA) Standards and, while not commercially used for some time, is being reconsidered. However, ACC is weak against copper-tolerant fungi and future disposal might be regulated.

**Copper azole** Copper azole, either with (CBA) or without added boron (CA), consists of the biocides copper(II), boron, and tebuconazole (or propiconazole). CBA is one of the newer nonarsenical water-based preservatives for aboveground and ground-contact applications in Europe, the United States, and Asia. CBA is listed in the AWPA Standards as CBA-type A, with a copper : boric acid : tebuconazole composition of 49 : 49 : 2. A modified formulation without boron (CA-type B) has just been introduced in the United States. CAs are formulated with relatively expensive ethanolamine to minimize metal corrosion at treating facilities and improve penetration and distribution of the biocide within wood.

**Cu-HDO** The copper bis-(*N*-cyclohexyldiazeniumdioxy) system (Cu-HDO, CX) consists of the biocides Cu-HDO, additional uncomplexed copper (II), and boron. The Cu-HDO portion exhibits good stability, but the borate component can quickly leach and the uncomplexed copper is also subject to some leaching. A water-based Cu-HDO standard has just been developed by the AWPA for aboveground applications, CX-type A, and 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 copper(II) carbonate and the remaining 6.4% copper as Cu-HDO, with a CuO : boric acid : HDO ratio of 4.38 : 1.75 : 1. A similar product is one of the major preservatives in Europe for aboveground and ground-contact applications.

**Copper citrate** Copper citrate (ammoniacal copper citrate (CC)) is formed by the combination of copper and citric acid. It is effective against most wood-destroying fungi and insects but weak against copper-tolerant fungi and susceptible to copper leaching. Thus, CC may be best suited for aboveground applications. Only small amounts are available in North America.

**Copper quaternary ammonium compounds** Copper quats (alkaline copper quat (ACQ), amine copper quat, ammoniacal copper quat) combine the biocides copper(II) and one of the quaternary ammonium compounds (quats) discussed below, usually with a CuO : quat ratio of 2 : 1. These are formulated in aqueous solutions using ammonia or a relatively expensive organic amine. Three types of ACQ are available in North America, with various formulations and types of quat. ACQ has been available in the United States and Australia for about 10 years and even longer in Europe and Japan. ACQ may soon be one of the major preservatives in North America.

**Oxine copper** (Bis)-copper-8-quinolinolate (oxine copper, copper-8, Cu-8) is an organometallic with very low acute toxicity to mammals, excellent stability and leach resistance, broad activity against decay fungi and insects, and has been used for minor applications for over 30 years. It is insoluble in water and most organic solvents and thus difficult to formulate. An oil-soluble formulation uses relatively expensive nickel-2-ethylhexoate as a cosolvent. A water-soluble 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. A small volume of Cu-8 is used in the United States for aboveground applications and for sapstain and mold control, and minor amounts are sold as a brush-on preservative. The mono form of Cu-8 is being studied.

**Copper naphthenate** Copper naphthenate is an organometallic biocide made by combining copper (II) with naphthenatic acid mixtures. Copper naphthenate is relatively low cost and has been used for over 50 years for various applications in North America, including treating wood during World War II. It has low toxicity to mammals, broad activity against decay fungi and insects, is readily soluble in hydrocarbons, and has good stability and leach resistance. Since the 1990s some utility poles have been treated with copper naphthenate in North America. 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. Small amounts of copper naphthenate are also sold over the counter to homeowners. Copper naphthenate imparts a green color to wood; for applications where color is objectionable the slightly less effective zinc naphthenate can be used. A water-based system is available in North America for brush-on (nonpressure) applications, and may be available soon for pressure treating.

**Polyphase™** 3-Iodo-2-propynylbutyl carbamate (IPBC, Polyphase™) is an organic biocide with low toxicity to mammals, is readily soluble in hydrocarbon solvents, has a broad range of activity against decay and mold fungi, but has no activity against insects and may be slowly degraded. In the United States, as a sole biocide IPBC is currently used for millwork-type applications, and IPBC was combined with the insecticide chlorpyrifos as an oilborne treatment for aboveground beams, etc. A formulation containing IPBC, propiconazole, and tebuconazole has recently been introduced as a millwork preservative in the US. In Europe many combinations of IPBC and propiconazole, or IPBC, propiconazole and tebuconazole, solvent- or waterborne, are used in aboveground applications. IPBC is the active ingredient in many brush-on systems sold in North America, and the combination of IPBC and DDAC is used for sapstain and mold control.

**Quaternary ammonium compounds** Several quaternary ammonium compounds (quats) are available, including didecyldimethylammonium chloride (DDAC, Bardac 22$^{TM}$) and other similar dialkydimethylammonium chlorides with $C_8$–$C_{14}$ alkyls, and the alkyldimethylbenzyl ammonium chlorides (alkyl benzyldimethylammonium chlorides, benzalkonium chlorides, ABACs, ADBACs), usually sold as a mixture with $C_{12}$–$C_{18}$ alkyl groups. The quats have very low toxicity to mammals, 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 used alone may not be adequate. Another disadvantage is that quats, as surfactants, make exposed wood wet 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 ACQ, discussed above, and DDAC plus IPBC is a commercial sapstain and mold agent. Quats will undoubtably continue to be considered in the development of new preservative systems.

A relatively new quat analog is an oligomer of alternating quat and borate ether units, commonly called polymeric betaine (didecyl-bis(2-hydroxyethyl) ammonium borate or didecylpolyoxethylammonium borate). Both the quats and borate ethers can bind to wood and, thus, the structure of the active ingredient changes when exposed to wood. The oligomeric structure makes the borate relatively less susceptible to leaching. Being composed of both quats and borates, polymeric betaine is active against both decay fungi and insects. Several water-based polymeric betaine systems are commercially available in Europe, including systems with polymeric betaine alone or combined with an insecticide for above-ground use, or with co-added copper for ground-contact applications.

**Synthetic pyrethroids** The synthetic pyrethroids (Permethrin, Bifenthrin, Cypermethrin, Cyfluthrin, and Deltamethrin), analogs of chrysanthemum-derived terpenoid pyrethrins, have low toxicity to mammals, exhibit good efficacy against insects (but are not fungicidal), and are soluble in many hydrocarbon solvents. (Only the structure of Permethrin is shown in **Table 1**.) In the United States research on the combination of a synthetic pyrethroid and fungicide has been conducted but no commercial applications currently exist. In Europe several combinations of a synthetic pyrethroid and other biocide(s) are available, including the quat benzalkonium chloride combined with permethrin and tebuconazole, or a cypermethrin and tebuconazole mixture.

**Tributyltin oxide** 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 aboveground treatment for millwork and related applications in many countries. However, it undergoes slow dealkylation which reduces its fungicidal properties. Consequently, TBTO has been used for reduced decay applications such as millwork in Europe and the US.

### Biocides with the Potential to Preserve Wood

Some biocides are being evaluated for wood preservation. Most of these are already registered and labeled for non-wood agricultural applications. Examining the potential of registered agrochemicals to protect wood has the advantage that the cost of label expansion is less than the expenditure required to develop, test, then register and label an entirely new biocide developed for only the relatively small wood preservation market. Potential biocides shown in **Table 2** are briefly discussed below.

**Chlorothalonil** Chlorothalonil (2,4,5,6-tetrachloroisophthalonitrile) is an organic biocide with very low toxicity to mammals, broad activity against decay fungi and insects, relatively low cost, and good stability and leach resistance in wood. A major research effort in the 1990s examined chlorothalonil as an alternative for penta. However, the poor solubility of chlorothalonil in most organic solvents made formulation difficult and interest has waned.

**Copper bis(dimethyldithiocarbamate)** Copper bis (dimethyldithiocarbamate) (CDDC), with the mono form preferred, is formulated with copper(II), ethanolamine, and sodium dimethyldithiocarbamate (SDDC). Since copper reacts rapidly with SDDC to form an insoluble complex, a two-step treating process is required. This results in a stable preservative with good activity against most wood-destroying organisms, but the dual treatment increases the cost.

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

**Kathon 930™** The isothiazolone 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (Kathon 930™) is a biocide with moderately low toxicity to mammals and broad activity against decay fungi and termites. It 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 aboveground and ground-contact applications, but no commercial formulations are currently available. Other isothiazolone analogs are used for short-term control of mold and sapstain fungi on wet, freshly treated lumber.

**Fipronil** Fipronil (5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethyl)sulfinyl]-1*H*-pyrazole-3-carbonitrile) is an $\alpha$-phenyl pyrazole-type insecticide. When combined with a fungicide it has been examined as a wood preservative.

**Imidacloprid** Imidacloprid (1-[(6-chloro-3-pyridinyl)methyl]-*N*-nitro-2-imidazolidinimine) is a neonicotinoid insecticide. Field tests in the United States showed that imidacloprid had much greater efficacy than chlorpyrifos in protecting wood against termite attack, but it may be degraded relatively rapidly.

**Polymeric xylenol tetrasulfide** Polymeric xylenol tetrasulfide (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 so far in marine and ground-contact tests currently under way. Being an oligomer PXTS should have minimal leaching, which would reduce the retention necessary for long-term protection and be suitable for environmentally sensitive applications. PXTS has exhibited low toxicity to mammals in tests to date.

2-(**Thiocyanomethylthio) benzothiazole** 2-(Thiocyanomethylthio) benzothiazole (TCMTB, Busan 30™) is an organic biocide with a broad range of activity against both fungi and insects. It is readily soluble in hydrocarbons and exhibits good leach resistance in wood, but it is susceptible to biodegradation.

## Trends in Biocides Used to Preserve Wood

Wood preservation is rapidly changing. In North America CCA is currently the most important preservative–by far–for residential applications, and penta, creosote, and CCA are used for industrial applications. However, CCA will be restricted to industrial applications starting in 2004 in North America, and residential lumber will be treated with alternative second-generation waterborne copper: organic systems which are copper-rich and possibly the older ACC system. ACQ, CA, Cu-HDO, copper and polymeric betaine, and possibly CCB and related copper/chromium systems, will probably be the main systems in Europe, Japan, and/or North America for the next several years. The newer preservatives are relatively expensive, more corrosive to metal fasteners, and apparently leach more copper than CCA-treated lumber. While these problems are avoided by the copper/chromium systems such as CCB and ACC, disposal concerns may soon lead to restrictions on chromium-containing systems. Another problem is that all lumber which has been treated with a waterborne preservative system and not yet redried (including wood treated with CCA) is susceptible to growth of molds and sapstains on the lumber surface, but the organic amine in many of the new copper-based preservatives may exacerbate mold growth. (Many preservative formulations also contain a biocide for short-term control of molds and sapstains on wet, freshly treated lumber.) New preservatives may also require more attention in the treating plant than CCA; indeed, many new systems have initial problems. Copper has some environmental and disposal concerns, and systems with relatively low copper levels plus one or more organic cobiocides might be eventually required. Alternatively, totally organic biocides might be mandated, a trend already happening in some European countries. Borates are being used to a greater extent for nonleaching residential applications.

Disposal of treated wood is, or will shortly be, a major issue in many countries and could be a principal factor determining which biocides are permitted. An intriguing possibility being studied in Europe is to utilize organic biocides which slowly degrade, and would protect wood for a specified time but then allow the product to be safely disposed of. The recycling of treated wood, such as grinding CCA-treated lumber into particles for particleboard furnish, may prove difficult due to liability concerns.

Many new organic biocides are extremely effective against some, but not all, wood-destroying organisms. Thus, future totally organic preservatives will likely consist of a combination of biocides, possibly including other nonbiocidal additives such as water repellents, to enhance the biocide's efficacy. Any synergism observed by combining multiple biocides would be a bonus. A preservative system used to treat lumber for residential construction will likely be water-based, but most organic biocides are not water soluble. Consequently, stable emulsions must be developed. Another problem is that organic biocides can be degraded by various chemical, biological, thermal, and/or photolytic mechanisms and thus rendered inactive; in contrast, the inorganic metals, such as the components in CCA, are 'permanent' and will only undergo a change in oxidation state. Thus, developing economical and effective totally organic systems, especially for locations with severe decay and/or termite conditions, will be a difficult, long-term, and costly process. At the present time no totally organic, aqueous-based system capable of protecting ground-contact wood for residential applications in the United States has even been proposed to a regulatory agency.

The high cost of new biocides, along with environmental concerns, will undoubtedly result in efforts to reduce the biocide level in totally organic systems to about 0.4% to 0.01% mass per mass of wood. By contrast, the traditional CCA and penta systems use about 1% mass per mass. Since wood is inherently variable this results in lumber from one commercial treating charge having a wide range of within- and among-board biocide retentions. With the highly effective traditional systems biocide retention variability is not serious, but it may become an important factor with the newer systems which have lower retention levels, and possibly less efficacy, than CCA or penta.

The total yearly cost to US homeowners due to fungal and termite attack is estimated at about US$5 billion. Some of these costs could be avoided by better design and construction techniques, but wood preservatives will still be needed for many applications.

## Formulations

Once a particular biocide(s) has been selected it must be formulated into a preservative system suitable for commercial applications, in which the active ingredient (the biocide) is combined with various inactive compounds. For treating solid wood and many composites, the biocide must be dissolved in a solvent (the carrier) or an emulsion developed. For industrial applications a heavy or light organic solvent, or water, can be used. Better efficacy with organic biocides is usually obtained with heavy oils, which by themselves often exhibit some biocidal activity and impart water repellency. For residential applications most systems are water-based; a light hydrocarbon is feasible but not likely due to cost and solvent emission issues. Since most organic biocides are not soluble in water an economical and stable oil-in-water emulsion must be developed.

Other characteristics of a viable preservative formulation, especially for residential applications, include:

- low cost
- good efficacy
- broad activity
- good permanence under long-term use
- no significant effect on wood strength
- low or no odor
- not corrosive to metal fasteners
- good penetration
- safe to handle and use
- leaves wood paintable and with an attractive appearance
- allows the wood to be disposed of or recycled at the end of the product's life
- capable of being concentrated (for shipment)
- formulated using only registered biocides.

## Standards and Organizations that Set Specifications

Once a preservative system formulation has been developed it is subjected to various tests with the results submitted to the appropriate standard-producing organization. Many organizations worldwide help set standards. In the United States over 10 organizations are involved to some degree in wood preservation; the major US organizations which develop standards are the AWPA and the American Society for Testing Materials (ASTM). The AWPA and/or ASTM Standards specify the formulations and retentions of various preservative systems for a wide variety of applications, as well as penetration requirements, treating processes, analysis procedures, laboratory and outdoor efficacy evaluation tests, etc.

A proposal of a new wood preservative system submitted to the AWPA for standardization typically includes the exact formulation, safety and health aspects, and results from various laboratory and field tests on corrosion, leaching, efficacy, etc., with the proposal listing the desired application(s) and retentions. The proposal is subjected to a peer review process by various industrial, governmental, and academic professionals, with an initial period of back-and-forth written questions followed by oral discussion at an AWPA meeting and then further time for additional written comments. If the proposal is accepted AWPA Technical Committees develop specifications that list the minimum requirements covering specific wood products recommended for a given preservative. Sponsors of the preservative system are required to submit periodic updates of long-term efficacy data generated in outdoor exposure trials. Standard development by organizations in other countries may follow a different format, but all are designed to ensure that the consumer obtains a reliable and safe product.

## Treatment Processes

Over-the-counter wood preservatives are generally brushed on by homeowners and only provide short-term protection. Control of sapstain and mold in green (never dried) lumber is accomplished by dip- or spray-treating with aqueous formulations. Millwork is generally treated by dipping or spraying dried wood. Most wood products are treated by a vacuum/pressure process, which gives the high loading and uniform penetration necessary for good quality control and long-term performance. In this process the wood product is usually first dried so that some or all of the free water in the cell lumen is replaced with air. The dried wood is placed in a pressure-treating cylinder, a vacuum drawn, then the preservative solution added to the cylinder so that the wood is fully immersed. Pressure is then applied to force the solution into the porous wood, with the preservative solution filling some or all of the lumen air-void volume; a vacuum may be drawn as a final step. The pressure treatment processes have basically remained the same for many years.

## Preservation of Wood Composites

Most preservatives are used to treat solid wood products such as lumber, ties, poles, etc., but the protection of wood composites is increasingly important. The treatment of composites involves special considerations. Generally, the furnish used to make wood composites is either treated with a biocide prior to manufacturing (preprocess) or a biocide is added during manufacture (in-process), or the composite is treated after manufacture (postprocess). The particular method and biocide system depends on the composite.

An example of a preprocess method is gluing lumber, which had been previously treated with CCA, into glulam beams. This process is only used with a few wood composites, using preservatives that do not negatively affect the adhesive. Postprocess treatment of an already manufactured composite is used where treatment will not adversely affect the product, and usually involves composites manufactured from lumber or veneer. In-process, where the biocide is added to the furnish just before mat formation and/or pressing occurs, is used where a postprocess treatment will cause undesired swelling and/or delamination of the composite and is usually practiced with composites manufactured from flakes, particles, or fibers. Postprocess treatments use standard preservative systems, are relatively easy and require no modification of the manufacturing process, but can result in only the outer shell being treated and some dimensional changes and strength loss. The in-process method gives protection throughout the composite, but the preservative can interfere with the adhesive and thermal degradation of organic biocides might occur during hot-pressing.

Because of its low cost, relatively good leaching properties, broad activity against a wide range of wood-destroying organisms, low toxicity to mammals, and good thermal stability, zinc borate has become one of the principal biocides used to treat in-process composites. Wax-based water repellents, either alone or in combination with a biocide, are also used.

## Naturally Durable Woods

The heartwood of some woods is naturally resistant to biodegradation. Commercially available durable woods include western red cedar, redwood, and cypress in North America, larch and pine heartwood in Europe, some woods from tropical forests, some eucalypts in Australia, etc. A major drawback is that most of these woods are not highly durable and may have a relatively short service life in certain applications or locations. Also, the availability of durable woods is not equal to the volume of pressure-treated wood produced in North America. Finally, some lumber with nondurable sapwood can be mixed in, durability varies greatly among and within trees, and the heartwood extractives which impart durability are often toxic or irritants.

## Nonbiocidal Additives to Enhance Biocide Efficacy

In addition to protecting wood, an ideal wood preservative system should improve the weathering characteristics by reducing water sorption. Consequently, the addition of water repellents to wood preservative systems is desirable. Besides improved weathering, durable water repellents enhance the biocide's efficacy by reducing leaching and lowering the moisture content of exposed wood. Water repellents are usually benign and can be extremely cost-effective. For example, most water repellents are wax- or oil-based and, on a weight basis, are about 100-fold cheaper than most organic biocides.

Lumber treated with several water repellent and preservative combinations is available in North America, and linseed oil-treated wood is being studied in Europe.

It is well known that decay fungi utilize free radicals generated by metals and/or organometallics to degrade wood. This, and the knowledge that extractives in durable woods have excellent antioxidant and metal chelating properties, suggested that antioxidants and/or metal chelators might help protect wood against fungal attack. Laboratory experiments have shown that antioxidants or metal chelators alone provide little protection to wood, but when combined with organic biocides enhance the efficacy of all biocides studied. Ground-contact and aboveground outdoor exposure trials are now under way and results so far are promising. This approach will likely be suitable only with totally organic systems.

Other possible additives include the in situ polymerization of nonbiocidal monomers. A portion of the monomers may covalently bond to the wood structural components to make the wood both more hydrophobic and impervious to enzymatic degradation. A similar concept involves reagents which form ester or ether linkages with the polysaccharide hydroxyls. Alternately, a resin could be impregnated into wood followed by polymerization. However, these treatments are expensive and require careful control and monitoring and so far have limited applications.

## Thermal Modification of Wood

In the past decade European researchers have reexamined the thermal modification of wood. As a result several processes have been developed and commercial production of heat-treated wood is growing rapidly. Generally, lumber is heated to at least 180°C in a nonoxidizing atmosphere. This causes some chemical degradation of the wood and, consequently, the wood has some decay resistance but mechanical properties are reduced. Also, greatly reduced hygroscopicity gives the lumber improved weathering characteristics. Although the durability of heat-treated wood is not equivalent to pressure-treated wood, it is suitable for low-hazard, nonstructural, above-ground applications.

## Biocontrol

Another biocide-free approach is to use microorganisms that are antagonistic to wood-degrading fungi and insects. This bioprotectant approach has been marketed in Europe to a limited degree, but there are some concerns about long-term effectiveness. Based on research to date, it appears that the most promising use for this concept is to control sapstain and mold fungi where only short-term protection is required.

*See also*: **Pathology**: Heart Rot and Wood Decay; Insect Associated Tree Diseases. **Wood Formation and Properties**: Biological Deterioration of Wood.

## Further Reading

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