Chemical Wood Preservative Systems in North America

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Many chemical wood preservative systems are available in North America. The particular system and the retention employed depend on the end use (industrial, agricultural, or residential), application (residential aboveground exposed, industrial ground-contact, marine, etc.), treatment method (dipped, painted, pressure treated, in-process treated, etc.; see Chapter 2), and the decay hazard and wood-deteriorating microorganisms in the particular area.

As mentioned in Chapter 1, a wide variety of organisms can attack and degrade wood. Thus, a wood-preservative system must exhibit broad spectrum efficacy during the long service life expected from treated wood. Other factors and characteristics that determine the viability of candidacy wood preservatives, especially for residential applications, are as follows:

- Cost effectiveness
- Low mammalian toxicity
- Water solubility/formulation
- Low vapor pressure
- Permanency in wood
- Waste product disposal characteristics
- Low odor
- No effect on wood strength properties
- Effect on wood surface characteristics.

Economics and broad spectrum effectiveness were the most important factors in the twentieth century when commercializing wood preservative systems. However, governmental regulations and environmental, health, and disposal issues have also become important.

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For treating solid wood products and most composites, the preservative must be dissolved or dispersed in a liquid carrier. For industrial and agricultural applications, the preservative systems can be formulated in an oil carrier, either light organic solvents or heavy oils. Heavy oils also provide some efficacy against basidiomycete but not soft-rot fungi and, further, reduce the leaching potential of organic biocides (e.g., Nicholas et al. 1990) compared to the light organic carriers. For exterior applications, the petroleum odor of heavy oils is not objectionable. For residential applications, almost all preservatives are formulated in a waterborne solution. This avoids potentially unpleasant petroleum odors or stains; furthermore, the water carrier has no fire hazards. However, if the biocide(s) is not soluble in water, as are most organic biocides, the preservative system must be formulated using sophisticated oil-in-water emulsion or submicron-particulate dispersion technologies.

Acceptable products for the particular service conditions that a treated wood product will be exposed to, and thus the organisms that could attack the product, are specified by the Use Category (UC) system in the American Wood Protection Association (AWPA) Standards (AWPA 2010) as described in Chapter 2.

North America covers a large area with diverse climates and, consequently, the deterioration hazard can vary. In aboveground applications, the wood must be moist and relatively warm for decay fungal spores to germinate and become successfully established; thus, the highest decay hazard will occur in warm and moist areas such as the southeastern United States. Wood in ground contact will remain wetter longer than aboveground wood; soil contains nutrients to help promote decay; and actively growing fungal mycelia exist in soil, rather than requiring fungal spores that must germinate. Further, the subterranean termites that occur in the lower two-thirds of the United States can more readily attack lumber in ground contact than aboveground. Wood in ground contact will have a higher deterioration hazard than wood in aboveground use in the same area, so higher retentions or more effective wood preservatives are required. The AWPA deterioration zone map shows regions ranging from 1 (low) to 5 (severe). Further, the microclimate can vary in adjacent areas, such as on a deck containing flower pots that are frequently watered, creating very moist conditions in the wood beneath.

This chapter covers the currently standardized chemical wood preservative systems in North America. The systems first discussed are the older systems; then the current, waterborne, non-arsenical, copper-based residential systems; and, finally, the newly standardized, totally carbon-based systems for aboveground residential applications.

3.1 First-Generation Systems

Creosote, developed about 200 years ago, is a viscous, coal-tar distillate, which consists of a complex mixture of over 200 organic compounds, primarily polyaromatic hydrocarbons along with some other phenolic and basic compounds. The composition and amount of each compound depends on the coal feedstock and the distillation process. Creosote is heavier than water and has a boiling range that begins at about 200°C. Creosote can be used whole or diluted with petroleum oil. It is usually heated to lower the viscosity and the creosote liquid is then pressure injected into the wood. Creosote accounts for about 15% of the total treated-wood market in North America and is primarily used for utility poles, marine pilings, and crossties; it is a restricted-use pesticide.

Pentachlorophenol (penta), an inexpensive chlorinated phenol, was developed as an alternative to creosote in the 1930s. It is typically dissolved in a heavy or light oil carrier and is mainly used to treat utility poles and crossarms. Heavy oil carriers provide additional protection against basidiomycetes, but not soft-rot fungi, and also reduce depletion (Nicholas et al. 1990). Penta currently accounts for about 5% of the total North American treated-wood market and is a restricted-use pesticide.

The major wood preservatives in the last half of the twentieth century were the waterborne arsenicals, principally chromated copper arsenate (CCA), but also ammoniacal copper zinc arsenate (ACZA). Although waterborne, CCA undergoes a complex series of fixation reactions that make it highly leach resistant. Further, being waterborne, CCA leaves the treated wood product clean and paintable. CCA is highly effective against essentially all wood-destroying organisms except those that inhabit but do not consume wood as a food source. The efficacy and waterborne characteristics led to a rapid increase in the use of CCA-treated wood in the residential market. Consequently, during a 40-year period up to 2004, the industrial volume of treated wood remained about the same, while the residential market grew greatly and now accounts for about 70% of the total treated-wood market. CCA-treated wood products, such as decking, plywood, and fencing, were used in over 95% of the residential market. The registrants voluntarily withdrew CCA from residential applications in 2003 in North America, but this system is still registered for industrial and some agricultural applications. CCA is currently used to treat about one-third of the utility poles in North America, along with other industrial and agricultural applications, and it is still permitted for some minor residential applications such as timbers for the permanent wood foundation. ACZA is employed to treat refractory (hard to treat) western softwood species for industrial applications.

The above systems are very effective for long periods, making them extremely competitive compared with non-wood construction materials. Thus, they dominated the wood preservation market in North America. Other minor first-generation systems include copper ligands, organometallics, and totally carbon-based systems.

Copper naphthenate is a copper-ligand biocide made by complexing copper(II) with the petroleum by-product naphthenic acids. It was briefly employed as a wood preservative during WWII and came back into use in the 1980s as an alternative to penta. It has low mammalian toxicity, broad activity against decay fungi and insects, is readily soluble in hydrocarbons, and has good stability and leach resistance. Starting in the early 1990s, about 3% of pressure-treated utility poles and most of the nonpressure fence posts have been treated with oil-borne copper naphthenate, and many utilities include this system as an alternative to penta or creosote. A thick paste of copper naphthenate and borate or fluoride is also available for remedial treatment of utility poles. A waterborne formulation has long been available over-the-counter to coat the ends of treated lumber cut from refractory western softwoods. A waterborne copper naphthenate system has also recently been standardized by the AWPA for the large pressure-treated residential market. Copper naphthenate leaves treated wood with a green color; for products where no color is desired, the less effective but clear zinc naphthenate can be employed.

(Bis) copper-8-quinolinolate (oxine copper, Cu-8) is an organometallic biocide with extremely low acute mammalian toxicity, excellent stability and leach resistance, and broad activity against decay fungi and insects. Cu-8 is currently the only biocide listed in the AWPA Standards and the CFR (Code of Federal Registration) for applications where the treated wood will come into contact with foodstuffs, such as for fruit and vegetable bins. Minor levels are used in North America for aboveground applications and sapstain or mold control, and small amounts are sold over-the-counter for brush-on applications.

Trubutyltin oxide (TBTO) is another organometallic biocide that exhibits good activity against both fungi and insects, is easily formulated with hydrocarbons, does not color the wood or reduce its strength properties, and has good leach resistance. It is used as an aboveground solvent-borne or oil-borne treatment for millwork in North America and Europe. However, it undergoes relatively slow dealkylation with subsequent reduced bioactivity and so it is most suitable for low-hazard areas, such as colder areas of northern Europe. In North America, TBTO is still registered for millwork, but it has largely been replaced by other chemicals. For example, 3-Iodo-2-propynylbutyl carbamate (IPBC, Polyphase™) is an organic biocide with low mammalian toxicity. It is easily formulated in hydrocarbons and has good efficacy against decay fungi and molds. However, IPBC has no activity against insects and, over time, is slowly degraded in wood (Schultz and Nicholas 2003). IPBC has been used to treat some millwork in North America and has been employed for aboveground treatment of beams when combined with an insecticide, but its most common use is for mold and stain protection. In Europe, IPBC is combined with other fungicides and/or insecticides for aboveground applications in low-hazard areas.

3.2 Non-Arsenical Copper-Based Systems

The industry decision to limit CCA use to non-residential applications in 2004 led to a sharp rise in the use of waterborne systems containing copper(II) (hereafter copper) solubilized with an amine or ammonia, with an organic co-biocide to control copper tolerant fungi. The soluble amine copper systems, by virtue of their higher copper levels, alkalinity, and lack of chromium, behave differently than CCA in terms of reactions with fasteners and mobility in aquatic environments applications. A thorough discussion of the mobility of alkaline copper systems can be found in Chapters 8-10. Alternatives to the solubilized copper formulations have recently been commercialized, where basic copper carbonate is milled to submicron particles which are suspended or dispersed in water, called micronized, dispersed or particulate copper (Freeman and McIntyre 2008). Reduced metal corrosion and copper leaching occurs in wood treated with micronized or particulate copper formulations (see Chapter 9). Products treated with particulate copper formulations have been commercially available since 2006 in North America. As with all new systems, it is important to understand the efficacy of soluble versus particulate copper systems, and these formulations are still being evaluated as more data becomes available (e.g., pro: Freeman and McIntyre 2008; or con: Schultz and Nicholas 2010).

All preservatives must be used at levels capable of protecting the wood for a reasonable period of time. In most cases, this time frame is a minimum of 20 to 30 years, but often extends for a much longer period. At the same time, wood is a variable material and treatments will produce a range of preservative retentions. As a result, target retentions are several times the actual protective level to ensure that the vast majority of the wood is treated to a level that will confer protection. There has been a recent move to lower these retentions. While this could have a strong positive outcome in terms of leaching risk, there must be performance data to support these moves. Any reductions in treatment levels must be balanced against any increased risk of early failure. These early failures could result in premature replacement that might actually result in more disturbance of an aquatic system.

The first systems for protection of wood for residential applications that were used after the CCA registration was changed contained soluble alkaline copper plus quaternary (quats) ammonium compounds (ACQ). ACQ was first standardized in North America in 1992, but was only used to a limited extent. It quickly became the major system employed in North America in 2004 as a CCA alternative. Both alkyl and benzyl derivative quats are available. Quats have broad activity against a wide variety of decay and mold fungi and insects and low mammalian toxicity and, while water soluble, become relatively leach resistant through ion exchange reactions with the wood. However, quats can be degraded by bacteria and have only moderate biocidal activity. As a result, a co-biocide is necessary to provide sufficient protection (Freeman et al. 2006). Although the first quats used had a chloride cation, quats now have carbonate cations to reduce metal corrosion in the treating facility. This change had no effect on efficacy. A CuO:quat ratio of 2:1 is usually employed. Several formulations of solubilized copper quats or ACQs are available for treating wood. Wood treated with micronized copper quat (MCQ) became commercially available in 2006.

The other major copper-based preservative used for residential applications in North America are copper azole (CA) formulations, where copper is combined with relatively low levels of one or two of the highly effective azoles. The azoles, or more properly triazoles, are either tebuconazole or a tebuconazole-propiconazole mixture, with a 25:1 Cu:Azole ratio in the treating solution. Azoles have extremely high efficacy against most basidiomycete brown- and white-rot fungi but are ineffective against molds, soft-rot fungi, and insects. As a result, they are typically used in combination with copper or other co-biocides. Furthermore, azoles can be biodegraded by wood-inhabiting bacteria and molds, and the azole tebuconazole appears relatively weak against copper-tolerant compared to copper-sensitive fungi (Exner 1991, Buschhaus 1995). Azoles are easily formulated in hydrocarbons or as an oil-in-water emulsion for waterborne systems, and are relatively leach resistant. There are several formulations of solubilized CA systems that have been standardized in North America, including one that contains boron. Boron is an effective insecticide and fungicide, but is relatively quickly leached from exposed wood. Particulate or micronized copper systems with azole(s), known as µCA-C or MCA, are also available. Particulate copper systems can also be formulated with partial substitution of soluble copper for some applications.

Two other copper-based waterborne systems are commercially available in Europe and have been recently standardized in North America. Copper bis-(N-cyclo-hexyldiazeniumdioxy) (Cu-HDO, copper Xyligen, CX) consists of relatively low levels of Cu-HDO, additional uncomplexed copper, and boron. Cu-HDO exhibits good stability, but the borate is leached relatively quickly and the non-complexed copper also can leach. This system had good aboveground performance in research tests, but low efficacy in ground-contact in areas where copper-tolerant fungi were present. Polymeric betaine (didecyl-bis, 2-hydroxethyl ammonium borate, didecylpolyoxethylammonium borate, DPAB), 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 less prone to migrate. Additional borate can also be combined in the formulation, with the system called impralit-KDS.

3.3 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 long history of good efficacy against wood-destroying fungi and insects. Borates are not corrosive to metal fasteners, are colorless, the treated wood can be stained or painted once dried, and borates provide some fire resistance to treated wood. However, borates are easily leached in outdoor exposure and so are only standardized for indoor, non-exposed UC1 applications or UC2 exposure if the wood is painted. Borates are also used as a diffusible biocide for remedial treatment of millwork and related products.

Much research has been conducted to find a non-leachable borate system, but so far the results have not been satisfactory in terms of providing leach resistance while still retaining bioactivity. Several firms have claimed to have developed a borate/silicate process that fixes the borate so that treated lumber can be used in exposed applications, such as decking. However, there is no independent, long-term field-exposure data verifying the effectiveness of these so-called "fixed borate systems" in appropriate tests.

The boron systems are usually dissolved in water for wood treatment. Some wood composites are treated in a different manner, with the biocide in a solid powder form added to the wood furnish prior to the mat being formed and the composite pressed. The main preservative used for in-process treatment of composites is solid zinc borate.

3.4 New Organic Carbon-Based Systems

Although the copper-rich wood preservatives are non-arsenic and chromium-containing, copper must be used carefully in aquatic systems. Totally organic or carbon-based wood preservative systems for outdoor aboveground and/or ground-contact exposure (UC3 and UC4) have been available in low-decay hazard areas such as northern Europe for some time, and several aboveground systems were recently standardized in North America. In general, it appears that development of a suitable, effective system for aboveground residential use (UC3) is fairly straightforward. However, identifying an effective and economical carbon-based system for ground-contact (UC4) applications has proven more difficult. In part, this is due to the relatively long service life expected from treated wood products and the susceptibility of organic biocides to biodegradation by wood-inhabiting bacteria and other organisms, especially in applications where the wood can have a relatively high moisture content, such as in ground contact. In addition, the new agrochemicals, while extremely effective at very low levels, are generally effective against only a limited number of the many fungi and insects that can degrade wood. Thus, the new systems typically employ a mixture of two or three organic biocides to ensure broad efficacy.

Most of the organic biocides being examined as possible actives in wood preservative systems are already registered and commercially employed for agrochemical applications. This makes it easier to use these biocides for wood preservation, as most of the required toxicological testing has already been performed. The one exception is polymeric alkylphenol polysulfide (PXTS), which was developed as a creosote alternative for applications such as decking, railroad ties, and marine pilings. Polymeric alkylphenol polysulfide has a very low mammalian oral toxicity and, being an oligomer, relatively low mobility. PXTS is a dark-colored solid and, like creosote, must be heated or a diluent employed to lower the viscosity prior to pressure treatment. PXTS has been found to be effective in long-term outdoor tests under severe deterioration hazards, with retentions of 4 kg/m^3 and 16 kg/m^3 for aboveground and ground-contact applications, respectively. PXTS has been standardized by the AWPA, but is not currently commercially available.

Two waterborne, third-generation systems that have recently been standardized for aboveground only applications (UC1 to UC3) by the AWPA are PTI and EL2. PTI is an azole-based system with a mixture of tebuconazole and propiconazole with a very small amount of the insecticide imidacloprid. Imidacloprid, a neo-nicotinoid, is extremely effective at controlling termites and other insects, even at very low levels. However, it can migrate in wet wood and may also be biodegraded, and consequently depleted in exposed applications. Similar azole-based systems, but with a synthetic pyrethroid insecticide, such as permethrin, are available in Europe and Oceania.

Although very effective in aboveground applications, azoles alone are not suitable for ground-contact applications due to their lack of efficacy against soft-rot fungi and the biodegradation of the azoles by bacteria and ascomycete fungi. Azoles are currently the most common treatment for millwork in North America. EL2 is based on the isothiazolone fungicide, 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOI), which is combined with the insecticidal compound imidacloprid. DCOI has moderately low toxicity to mammals and the combination has broad activity against decay fungi and termites. It is readily soluble in hydrocarbons and exhibits excellent stability and leach resistance in wood in long-term testing in areas with high to severe deterioration hazard in both above ground and ground-contact applications. The EL2 preservative system uses patented waterborne polymer technology where the DCOIT active is absorbed and contained in dispersed polymer particles that carry the DCOIT active into the wood during treatment.

Other potential organic biocides include the fungicidal azole cyproconazole and the insecticidal neo-nicotinoid thiamethoxam. These are reported to have even greater activity than their highly effective analogues discussed above and are already commercially available and registered. Another potential biocide used for some time in agrochemical applications is chlorothalonil. This biocide has extremely low toxicity to mammals, broad activity against decay fungi and insects, and has good stability and leach resistance in wood. A major research effort in the 1990s examined it as an alternative for penta. The poor solubility of chlorothalonil in most organic solvents makes formulation for pressure preservative treatment of wood difficult. However, it may be possible to develop a non-traditional formulation, such as a dispersed particulate waterborne system.

3.5 Non-Biocidal Additives That Enhance Biocide Efficacy

Non-biocidal additives already added to some commercial systems include water repellents, often wax hydrocarbons that are formulated with an emulsion. Water repellents in aboveground lumber, such as decking, reduce the water sorbed during rainstorms and, thus, greatly reduce the decay potential. Furthermore, by reducing the amount of water sorbed by the treated wood product, less biocide is leached. Water repellents can also enhance the dimensional stability of lumber in aboveground applications. Water repellents are employed in many of the second- and third-generation aboveground systems.

Totally carbon-based systems have some concerns, including the biodegradation that organic biocides can undergo during their long service life, especially by microorganisms that inhabit but do not degrade wood, such as molds and bacteria. To address these concerns, scientists are studying benign additives based on the common fundamental knowledge that decay fungi employ metal-mediated free radical reactions to degrade wood. Thus, researchers examined co-adding benign and economical antioxidants and/or metal chelators to organic biocide systems (Schultz et al. 2008). These additives were found to increase the efficacy of organic biocides, often by two- or three-fold, in both laboratory and outdoor, long-term ground-contact and aboveground tests. Further, reduced depletion was found with several organic biocides when an antioxidant and/or metal chelator were employed.

It was recently hypothesized that the antioxidant properties of heartwood extractives interfere with the symbiotic microbe digestion of termites and, consequently, termites would avoid heartwood with high levels of extractives with antioxidant properties. This hypothesis was tested in the laboratory by treating wood with the benign and artificial antioxidants, where it was found that antioxidants did indeed deter termites and increased termite mortality (Ragon et al. 2008, Little et al. 2010).

Clearly, improving our understanding about how the various agents of deterioration function will ultimately help develop more targeted and rational approaches to wood protection. At the same time, it is important to remember that there are a broad range of potential wood degrading organisms and that many of these agents have physiologies similar to ours. As a result, we will continually search for systems capable of inhibiting organisms at increasingly lower dosages to minimize the risk to non-targets.

3.6 Standardization of Proposed Wood Preservatives

Any biocide used in the U.S. must be registered with the U.S. Environmental Protection Agency (EPA) under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), which insures that all products are suitable for the intended application; i.e., the benefits merit the risks. Furthermore, individual state agencies may have additional requirements. To register a bioactive compound, a company must conduct extensive toxicological and other health-effect tests, environmental fate studies, and a host of other tests. Once registered, the company then develops a “label” which, after acceptance by the appropriate regulatory agency, clearly lists the specific applications and quantifies the rates for which the formulated biocidal products can be legally used. Once a preservative system formulation has been developed, it is subjected to various laboratory and outdoor tests to determine efficacy in the proposed application(s), properties, including metal corrosion, leaching/depletion, penetration into the listed wood species, analytical procedures, etc. Generally, ground-contact field-efficacy data based on three years of exposure in at least two geographically different locations with high or severe deterioration hazard is required, provided comprehensive depletion data is also obtained. After sufficient testing, the results are then proposed to a standard-setting organization. The two main organizations that deal with standardizing new wood preservatives in the U.S. are the American Wood Protection Association (AWPA) and the International Code Council-Evaluation Service (ICC-ES). The processes by which the two organizations operate are different, but both involve review of performance and treatability data and are designed to ensure that the materials used to treat wood have acceptable levels of performance. Detailed descriptions of the standardization and biocide EPA registration processes are given in chapters of a recent book, *Development of Commercial Wood Preservatives* (Schultz et al. 2008).

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