

# Recent Patents and Developments in Biocidal Wood Protection Systems for Exterior Applications

Tor P. Schultz<sup>1,\*</sup>, Darrel D. Nicholas<sup>1</sup> and Craig R. McIntyre<sup>2</sup>

<sup>1</sup>Forest Products Laboratory, FWRC, Mississippi State University, Mississippi State, MS 39762 USA, <sup>2</sup>McIntyre Associates, Inc., 8565 E. Grandview Lake Dr., Walls, MS 38680, USA

Received: November 30, 2007; Accepted: April 1, 2008; Revised: April 7, 2008

**Abstract:** Wood products used in outdoor applications are treated with biocides to prevent biodegradation by many different fungi and insects. Environmental and disposal concerns have resulted in a rapid and dramatic worldwide shift from the older first-generation preservatives to copper-based systems for residential applications, where the copper(II) is complexed with an organic amine. In the last year the alkaline amine formulation has been partially replaced by microdispersed copper systems that offer several advantages. The current trend in wood preservation is directed towards combining two or more organic biocides in a waterborne formulation employing relatively benign and expensive agrochemicals, with non-biocidal additives sometimes added for increased efficacy and/or other benefits. This review discusses the patents and developments in the past 10 years in biocidal waterborne or solventborne wood protection systems for pressure-treating solid or composite wood products in exterior above-ground or ground-contact applications. Only totally organic systems and related recent developments are discussed, with the exception of microdispersions to formulate both metallic and organic systems.

**Keywords:** Agrochemicals, biodeterioration, dimensional stability, organic biocides, waterborne formulations, weathering, wood preservation.

## 1. INTRODUCTION

Wood products are extensively used in residential construction and other outdoor applications where the wood can be degraded by many different fungi [1], insects such as termites [2], or organisms in marine environments [3,4]. To prevent this, in applications where they can be degraded non-durable wood products should be treated with biocides. The wood preservation industry has recently undergone dramatic and rapid changes worldwide due to real and perceived environmental concerns and resulting governmental regulations [5].

About 60% of the total treated wood market resides in North America, with approximately 20% in Europe and 20% in Asia/Oceania. Overviews of future trends were recently written by Barnes [6] for North America, Asia/Oceania by Preston and Jin [7], and Leithoff *et al.* [8] for Europe. In the past 50 years in the large North America market, the volume of wood treated for industrial applications has remained relatively constant while the residential market greatly increased and now accounts for about 70% of the approximately 18 million m<sup>3</sup> of wood treated annually [9].

The protection of wood against the many organisms that can degrade it has unique problems. For above-ground and ground-contact applications, the biocides must be effective for many years against a wide variety of wood-degrading fungi and insects. Wood employed in marine applications has the most severe deterioration potential and wood in non-exposed indoor or sheltered applications that is rarely wetted by rain the least deterioration potential, but this review will

only cover terrestrial exterior applications. Also, the worldwide market for wood-preserving biocides is relatively small, about \$US 0.6 billion annually compared with \$36 billion for agrochemicals, so only limited R&D expenditures are justified [10,11]. Furthermore, the treatment cost is relatively small, about 15% of the total product cost, but if the product fails during the long service life the preservative supplier and/or treater is liable for the entire product. Therefore, wood preservation has a relatively small potential profit but carries a high liability potential [11].

The type and level of biocide(s) employed to treat wood for residential exterior applications depends on the intended application(s) and hazard potential of the particular area. Decay fungi require the wood to be wetted before fungal deterioration can occur, such as with rain for above-ground decking or wood in soil contact. Decay fungi also grow best in temperatures of about 15 to 40°C, although they can survive harsher environments. Thus, wood in above-ground applications in North America will have a higher potential for deterioration in warm and moist environments such as in the southeastern US than drier and/or colder zones. Further, wood in above-ground applications will generally only be attacked by spores of decay fungi that must germinate and become established before the wood dries out for the microorganism to survive. Conversely, wood in soil contact has a higher deterioration potential due to the moisture and essential nutrients in the soil, attack by established fungi rather than spores, and termites in many areas of the US. Thus, wood in ground-contact applications requires higher fungicidal levels than above-ground decking and an added insecticide for protection against termite attack.

Wood preservation has traditionally relied on only a few first-generation organic or metallic biocides that have a broad range of activity against the many organisms that can

\*Address correspondence to this author at Forest Products Laboratory, Box 9820, Mississippi State University, MS 39762-9820, USA; E-mail: tschultz@cfr.msstate.edu

degrade wood, are low cost, and remain effective for many years. The first-generation organic preservatives are creosote and oilborne pentachlorophenol (penta). These two systems leave the treated wood with an oily smell and visible surface residue that is acceptable for exterior industrial applications which is essentially their only market, and the oil carrier for penta provides additional protection against wood-destroying organisms. The first-generation metallics are the waterborne arsenicals, principally chromated copper arsenate (CCA), which was used for both residential and industrial applications. Being waterborne, CCA-treated wood has no oily smell or surface and so is suitable for residential applications, is very economical and CCA provides long-term protection in even the most severe environments and applications. Thus, in North America at the end of the century CCA accounted for about 80% of the total wood preservative market and over 95% of the large residential market.

Starting in the 1990s concerns arose over exposure and disposal issues of wood treated with penta, creosote, and the chromium and arsenic in CCA [9-14]. While extensive studies supporting or refuting these concerns have been conducted and the conclusions extensively debated [e.g. 15-17], the result was a rapid removal of penta, creosote, arsenic and/or chromium components from many preservatives in Europe and Japan and the introductions of the current second-generation preservative systems. About a decade later in North America, CCA was voluntarily de-labeled for residential applications and is now only permitted for industrial and agricultural applications with a few very minor exceptions. A few North America localities have restricted creosote in marine applications and penta has recently had a few minor limitations placed on its use, but at this time it appears that penta and creosote will continue to be approved for most traditional industrial applications for the near future.

The second-generation biocide systems that replaced CCA for residential applications in Europe, parts of Asia, and North America are the waterborne copper-rich systems that contain amine- or ammonia-complexed alkaline copper(II) and an organic co-biocide to control copper-tolerant fungi [18,19]. Concerns with these systems have recently arisen over relatively high levels of copper leaching and the resulting negative impact on aquatic ecosystems, corrosion of metal fasteners, different surface mold growth than observed on CCA-treated lumber, the relatively high cost of the organic amine employed in the formulation, the low level of copper that can be concentrated for shipment and the resulting high transportation costs, and the question over the long-term disposal of wood treated with metallic preservatives. In the past few years micron-sized copper(II) particles, usually copper carbonate, dispersed in water (microdispersed or micronized copper systems) have been developed that resolve many of the problems above. Microdispersed copper systems now account for an increasing volume of residential copper systems used in North America, and are discussed later.

The above concerns with copper-based systems have led three European countries to recently require totally-organic third-generation systems for residential applications, and this trend can be expected to accelerate. This has also been

driven by European initiatives on non-biocidal protection systems, regardless of economics or questionable environmental benefits. In North America, a few localities have enacted some restrictions on copper-treated wood, and historic trends forecast increasing restrictions or outright bans.

The general expectation among most professionals is that totally organic third-generation systems will eventually be required for residential exterior applications in the major world markets for treated wood. Alternatively, copper-poor systems based on much lower copper levels of the current second-generation systems or organometallic systems such as oxine copper or copper naphthenate may be permitted, but this possibility is considered unlikely.

Organic systems for residential exterior applications are already available in Asia and Europe, and all the major North American suppliers have recently submitted organic systems for approval or have just had systems approved. The organic biocides being employed or considered are, with only one exception that is discussed later, based on agrochemical biocides that are already labeled so that the considerable initial registration costs have already been borne [10]. However, in agricultural applications the biocide is expected to only control a specific fungus or insect and then quickly degrade, while in wood preservation the same biocide is expected to control a wide variety of decay fungi and/or insects and last for the many years of service life expected from treated wood. Therefore, only a few of the many agrochemicals available have properties suitable for wood preservation [18, 20-22]. Furthermore, organic biocides are biodegraded by both wood-degrading and wood-inhabiting but non-destroying microorganisms, which can deplete an organic biocide over time [23]. Another problem is that residential systems are waterborne, where the biocide is formulated in a water solution that is employed to pressure treat the wood product to ensure deep and uniform penetration of the biocide. However, most organics are not soluble in water so that microdispersions, microemulsions, or other sophisticated formulation chemistry must be developed. It is possible to treat residential wood with a light petroleum carrier or supercritical fluids, although commercialization of these formulations or processes is challenging. Finally, the new agrochemicals employed or being considered are generally effective against only a limited number of the many fungi and/or insects that degrade wood. Thus, many organic systems combine two or three biocides to ensure broad efficacy [5].

One of the most promising fungicidal biocides is the class known as azoles, or more correctly triazoles [18]. These compounds are active against Basidiomycete brown- and white-rot fungi and relatively benign, but have poor efficacy against soft-rot fungi and so are not effective in ground-contact. Azoles also have no insecticidal/termiticide activity. The azoles are very expensive per unit weight but their extremely high efficacy means that low levels are effective and, thus, they are cost effective. The leading azoles at this time are propiconazole, tebuconazole, and cyproconazole, with the first two already listed in the AWWA Standards [24]. Many of the new or proposed wood preservatives in North America for above-ground applications

employ one or more azoles. Another promising organic biocide that is listed in the AWWA Standards [24] but not currently employed is 4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one (DCOI, DCOIT, or Kathon 930™) [18]. This particular compound is an isothialozone, with simpler analogues used extensively in personal care products. DCOI has been extensively studied as a potential wood preservative both in ground-contact and above-ground applications where it was found to have good long-term efficacy against wood-destroying fungi, molds and termites, and excellent stability and leach-resistant properties. Research is on-going with this biocide, and a proposal for a new wood protection system based on DCOI was recently submitted to a US accrediting organization. Another class of biocides which is currently employed in commercial wood preservative systems and listed in the AWWA Standards [24] are the quaternary ammonium compounds, or quats [18]. These include didecyl-dimethylammonium chloride (DDAC) and its carbonate analogue, and the alkyldimethylbenzyl ammonium anions. Quats are used in a variety of household cleaning products and thus are very benign, are the organic component in the major copper-rich wood preservative sold in North America, are very inexpensive, have broad efficacy, and although water soluble once in wood quats fix through ion exchange mechanisms and so are leach resistant. However, quats have only moderate efficacy so they must be combined with other biocide(s) to adequately protect wood.

The above organic biocides are fungicides, some of which also have efficacy against termites and other insects. A class of insecticides that have no fungicidal activity are the large number of synthetic pyrethroids such as permethrin [18]. These compounds have low mammalian toxicity and exhibit good efficacy against insects. The extremely active neonicotinoids, including imidacloprid or thiamethoxam [18], are also only effective against insects. Many of the organic systems proposed for above-ground use in North America are based on one or two fungicidal azoles with an extremely small amount of imidacloprid. Finally, the low-cost fungicide chlorothalonil (tetrachloroisophthalonitrile) has been extensively studied and found to be leach resistant and effective against both decay fungi and insects. However, chlorothalonil has limited solubility in only a few organic solvents typically used for industrial wood protection systems and no water solubility and, thus, is difficult to formulate [18].

Certain non-biocidal process will also protect wood [25]. This review only covers biocidal systems and, thus, these non-biocidal methods are only briefly mentioned here. The heartwood of certain trees is naturally resistant to decay and/or insects. In North America commercial markets exist for redwood, western redcedar and cypress, but this lumber is relatively expensive, harvest restrictions limit availability, and the natural durability does not provide as much protection as commercially-treated lumber. Chemical modification of wood can also prevent fungal and/or insect degradation. Acetylated and heat-treated lumber is available in Europe and Japan, and additional acetylation [26] or furfurylation [27] plants are being built or considered in Europe and North America. However, since the cost of acetylated wood is relatively high and the process requires careful monitoring the market may be limited to high-end applications. Heat-

treated wood [28] has some decay resistance but it is not suitable where termites are present or for ground-contact applications and has greatly reduced strength properties. Thus, the North American market for heat-treated lumber is limited, and at this time no supplier is available. Other non-biocidal methods to protect wood include treating wood with various polymers or monomers that polymerize *in situ* [e.g. 29].

In addition to biodegradation, another challenge with lumber in outdoor exposure is that wood is an anisotropic and hygroscopic material that swells unevenly when wetted or shrinks as it dries. This can lead to undesired dimensional changes that result in splitting, bending or warping over time [30].

In this review we discuss the patents issued or applied for in the past 10 years and recent developments which, in our opinion, are significant. We focus on biocidal waterborne or solventborne wood protection systems for pressure-treating solid or composite wood products for exterior above-ground or ground-contact applications. Only totally organic systems and related developments are discussed, with the exception of microdispersions recently used to formulate metallic and organic systems. This is because it is unlikely that new copper-based systems could successfully compete against similar systems that are already available in Asia, Europe and/or North America, and increasing restrictions on metallic-treated wood are expected. Where more than one patent or application has been made from a company then only the latest patent or application is generally mentioned. Not covered are chemical wood modification and microbiological processes to protect wood, employing naturally-durable heartwood, borate systems, dip treatments to protect millwork, joinery and similar products for non-exterior low-hazard applications, solid preservatives (those systems that are not formulated as a liquid but as a solid) employed to treat some wood composites during manufacturing, biocides employed solely to prevent mold and stain growth, and systems to protect marine pilings.

## 2. RECENT PATENTS AND DEVELOPMENTS

### 2.1. New Biocides Developed for Wood Protection

As mentioned above, the relatively low market for wood biocides limits the R&D expenditures which a company can justify. Thus, with only one exception the new organic biocides being employed or considered for wood are all based on agrochemicals that have already been registered. The one exception is PXTS (polymeric alkylphenol polysulfide) [31,32], which was developed as a creosote alternative for applications such as railroad ties and marine pilings in Europe and North America. PXTS has a very low mammalian oral toxicity of  $LD_{50} > 5$  g/kg. Being an oligomeric compound it has low leaching potential and is environmentally benign. PXTS is a dark-colored solid and, like creosote, wood must be treated with PXTS at above-ambient temperatures or with a diluent to lower the viscosity. In above-ground tests PXTS has been shown to be effective at retentions of 4 kg/m<sup>3</sup> or higher after five years and in ground-contact tests good performance was obtained at retentions of about 16 kg/m<sup>3</sup> after seven years of exposure, with tests conducted in areas with severe deterioration

hazards [33]. PXTS has been standardized by the AWWA [24] but is currently not available.

## 2.2. Utilizing Synergism to Develop New Wood Preservative Systems

Employing synergism in wood preservation has received much attention recently [34]. If the combination of two or more biocides results in an unexpected or unique property, such as greater efficacy than expected, the system may be patentable. Patent protection is important in the wood preserving industry due to the high costs, risks, and the long time required to develop a wood protection system [11]. Other advantages are that the biocide levels can be reduced with resulting economic and environmental benefits, and a mixture of two or more biocides would likely have broader activity than one biocide and might control wood-inhabiting but non wood-destroying microorganisms such as bacteria that can biodegrade the organic biocide(s) present. (As mentioned above, only totally-organic mixtures are discussed. Further, we limit the discussion to systems where one or both of the organic biocides is currently employed or has potential in wood protection [18,20-22].

The azoles were mentioned earlier. Kumagaya [35] reported as synergistic the antifungal combination of cyproconazole and 3-iodo-2-propynylbuty carbamate (IPBC). IPBC has good efficacy against decay and mold fungi, is listed in the AWWA Standards [24] and is used in some wood applications, but its long-term efficacy is doubtful as the carbamate is reported to undergo degradation in outdoor long-term exposure. Pillay [36] claimed that the combination of propiconazole and 2-mercaptobenzothiazole (also called 2-(thiocyanomethylthio) benzothiazole; TCMTB; Busan 30™) was synergistic. TCMTB has a broad range of activity against both wood destroying fungi and insects, is leach resistant, but is susceptible to biodegradation. It has some minor applications in millwork and joinery. Ross *et al.* [37] found that combinations of azoles with IPBC, diiodomethyl-*p*-tolysulfone (also called Amical 48™), and amine oxides were synergistic. Amical 48™ has a broad range of activity against wood destroying fungi and insects and apparently good durability in wood in ground contact. Amine oxides have limited fungicidal efficacy but can enhance wood protection systems by non-biocidal means, as discussed later.

Hsu [38,39] received several US patents on the combination of DCOI with other biocides including IPBC, chlorothalonil, and TCMTB. Two of the co-biocides were discussed above, and chlorothalonil has long been studied as a wood preservative and found to have good long-term efficacy against both decay fungi and insects, is relatively benign, low-cost and leach resistant, but is difficult to formulate. Gaffney *et al.* [40] was issued a US patent on the synergistic combination of DCOI and a mixture of chlorinated isocyanurate.

Chlorothalonil and IPBC, both discussed above, was claimed by Winkowski *et al.* [41] to be a synergistic combination.

Rustenburg *et al.* [42] claimed as synergistic the combination of the azole cyproconazole and quats and Kovacevic [43] the combination of quats and isothiazolones such as DCOI.

Several biocide combinations of a pyrethroid and fungicide are commercially available in Europe. Matsugaki *et al.* [44] submitted a Japanese Patent application on the combination of pyrethroids and quats.

Fipronil (5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethyl)sulfinyl]-1H-pyrazole-3-carbonitrile) is an insecticide that has been examined as a wood preservative component. Uhr *et al.* [45] claimed that the combination of fipronil and nicotinic acetylcholine receptors would protect various materials including lumber.

## 2.3. Non-Biocidal Additives That Enhance the Efficacy of Wood Preservative Biocides

Non-biocidal additives have long been added to improve the efficacy of the biocides or provide other desired properties such as fire resistance, masking the odor of a petroleum carrier, color, etc. This review will only cover additives that enhance the efficacy of biocides.

One of the most common additives is adding a water repellent to above-ground biocide systems for premium decking [10]. The water repellent lowers the amount of moisture gained by the decking during a rainstorm and, consequently, the fungal decay potential is lower. The lower moisture level will also reduce biocide leaching and increase dimensional stability. Water repellents are usually based on petroleum wax, but low molecular weight hydrophobic polymers and aluminum stearate are also used. Water repellents are extremely inexpensive per unit weight and thus very cost-effective, and safe to humans and household pets. Water repellents may be even more essential with the third-generation totally-organic systems for above-ground applications [46].

Although water repellents for wood products have been commercially available for some time, several new patent applications have been recently submitted. Ashmore and Laganella [47] reported employing an aqueous mixture of a paraffin wax, non-ionic surfactant, and various organic preservatives. Shoshany and Shoshani [48] claimed that wood products would have improved properties by employing a wax suspended in water.

Amine oxides were mentioned earlier. While these compounds have only minimal efficacy against decay fungi, they provide water repellency and some mold resistance, help formulate organic biocides in water, and obtain a more uniform biocide distribution in treated wood [49-52]. Marks *et al.* [53] claimed synergism when combining amine oxides with IPBC and other biocides.

It has long been recognized that decay fungi employ free radicals generated by metal-mediated reactions to degrade wood. Furthermore, the extractives in naturally-durable heartwood have only moderate fungal activity but have excellent free radical scavengers and metal-complexing properties. Based on this knowledge, we combined various free radical scavengers (antioxidants) and/or metal complexing compounds with a variety of organic biocides [54]. In all laboratory and field experiments enhanced efficacy was observed when antioxidants and/or metal complexing compounds were combined with organic biocides as compared to the efficacy of the organic biocide alone [55-

57]. Furthermore, in one study with chlorothalonil, after about 4 years of ground-contact exposure in two areas with high or severe deterioration potential the co-addition of the low-cost and benign antioxidant BHT was found to reduce depletion of the biocide by about 50% [58]. This is significant as biodegradation of organic biocides by bacteria and other non-decay microorganisms that inhabit wood is viewed by many professionals a major problem with organic systems [23].

We were able to quickly identify a suitable antioxidant that was low cost, non-leachable, stable, and benign. However, selection of a suitable metal complexing compound was more difficult. While we were able to show enhanced efficacy with metal complexing compounds and organic biocides in laboratory decay tests [54], in outdoor exposure these compounds either leached over several years or would be unsuitable for commercial systems due to cost or toxicity [55]. Fortunately, we recently noted that resin acids provided enhanced efficacy in laboratory decay tests [59]. An additional advantage of the resin acids was that with a waterborne formulation good water repellency and dimensional stability was obtained [60,61].

As mentioned above, the role of non-decay microorganisms in the degradation of organic wood preservatives is a serious problem. Wallace and co-workers [23] found that various bacteria, especially the Gram negative proteobacteria *Pseudomonas*, could degrade organic biocides and reported that an unspecified reagent or method could help reduce biodegradation. Higaki [62] claimed that an organic preservative, such as cyproconazole, could be mixed with a biocide to control bacteria. Another possibility might be to employ ultra low silver levels of a few parts-per-million (ppm). Silver has some promise to protect wood against decay fungi and termites but would likely be uneconomical [63]. However, a few ppm of silver in wood may have good bactericidal properties [64, 65] against the microbes that can degrade organic biocides. The low levels of metal employed would likely not be a problem with disposal, as wood ash consists of various metal oxides.

#### 2.4. Waterborne Formulation Developments

As mentioned in the Introduction, residential wood preservative systems for pressure-treating lumber are all waterborne since homeowners desire treated lumber to have no oily odor or surface. However, with the exception of the quats and amine oxides all organic biocides being employed or considered for wood protection are not soluble in water. Thus, sophisticated formulation techniques are needed, such as oil-in-water emulsions. In contrast, for industrial applications like utility poles or railroad ties the product can be treated with either a waterborne or oilborne system.

Commercial formulations need to be concentrated for ease of shipment, the emulsion needs to be stable when the kick-back solution from the treated lumber is pumped back to the storage tank for re-use, be economical, and safe for the treaters and consumers. Finally, the emulsion can be only a few microns in size so that the biocide will pass through the small pits that connect adjacent wood cells. Recent emulsion patents and applications in organic wood preservations are available [66-69].

A recent development that has already had a large impact in wood preservation is the formulation of micron-sized metallic or organic particles suspended in water [70]. The price of the second-generation waterborne copper-rich systems is about three times that of the older CCA preservative, mainly due to the high formulation cost. Specifically, an organic amine must be complexed with the copper(II) to reduce metal corrosion in the treating facility. CCA, by contrast, employed chromium to virtually eliminate any problems with copper-mediated redox reactions and subsequent metal corrosion in the treating facility and with metal fasteners in the final application. Corrosion of the second-generation copper-rich systems is greatly reduced by employing copper(II) micron-sized particles [71-73], and the high cost of milling copper carbonate to microparticles is economically balanced by not having to employ organic amines. Another advantage is that the microdispersed system can be concentrated about three-fold more than the amine-formulated preservatives, thus reducing the shipping cost. Microdispersions may also be employed for organic biocides that are difficult to formulate in a water solution [74-76]. This technology has been rapidly commercialized in the past year, with fairly high volumes of micronized copper quat (MCQ) treated lumber now produced along with some micronized copper azole (MCA) treated lumber. Phibro-Tech and Osmose are the major companies with microdispersion patents or applications.

Another important formulation technique uses nanoparticles that are composed of a polymer and organic biocide which are impregnated into wood by a pressure treating process. The nanoparticles permit the controlled release of the biocide into the adjacent wood structure [77-79].

The oldest preservative system is creosote, a by-product obtained from the distillation of coal tar and still used to treat about 15% by volume of all wood in North America. Creosote is a thick black viscous liquid which is usually heated to lower its viscosity prior to pressure impregnation into wood, but some oozing occurs at the bottom of utility poles or from marine pilings to form a visible oil slick. Pigmented Emulsified Creosote (PEC) has been formulated to prevent these problems [80-82].

### 3. CURRENT & FUTURE DEVELOPMENTS

In this article, we have detailed the recent important developments in biocidal wood preservatives. Currently, wood preservation is a mature industry with limited potential for profit, and developments are usually not driven by economics or technology but by public perception and resulting governmental regulations. Finally, many consumers view wood products as a cheap and inferior product compared to the more expensive alternatives made from non-renewable resources such as plastic lumber. However, growing public environmental consciousness may result in increased awareness of the many green benefits of wood products. Specifically, treated wood is a sustainable, economical and effective building material that requires relatively little energy to manufacture, and trees sequester carbon dioxide as they grow. Further, employing treated wood reduces the need to harvest trees to replace untreated products that have deteriorated.

At this time, the current trend is towards developing environmentally-benign totally organic biocide systems. Alternatively, but not likely, copper-poor wood preservative systems might be approved. It is also possible to chemically modify wood to prevent fungal and insect biodegradation, as briefly mentioned in the Introduction. While some chemical modification facilities are being constructed the much higher costs, unavoidable environmental consequences, and need for careful process monitoring may limit this market to specialty, high-value products. Conversely, the development of totally-organic biocides for residential applications is more economical, and above-ground systems that are already developed can provide good service even in harsh environments provided sufficient organic biocide is employed and the biocide(s) remains effective over the many years of service life expected from treated wood. The efficacy of these systems can be further enhanced by employing water repellents, which also gives more dimensionally stable lumber which consumers are increasingly demanding. Some technology is also available to reduce weathering and photo-degradation, with research continuing in this area. Other non-biocidal additives, such as antioxidants or metal chelators, may also be employed.

The development of suitable totally-organic systems for ground-contact applications will be a bit more challenging, but some work is already underway in this area. Additives to enhance the biocides' efficacy and/or reduce biodeterioration by bacteria and other microorganisms may be important. Alternatively, it is possible that low-copper systems might be permitted for future ground-contact applications in North America. These could be based on the current copper-rich systems with formulation technology employed to reduce copper migration. Alternative systems might be developed based on organometallic systems such as oxine copper or copper naphthenate.

One problem with the new organic biocides is that their bioactivity and cost are relatively high; consequently, the levels being proposed are one to two orders of magnitude lower than those employed with the first-generation systems. This has made it difficult to accurately measure the biocide level and sophisticated analytical instruments are required. A second problem is that uniform macro- and micro-distribution of the biocide(s) within a treated wood product will be important.

Borates are extremely economical and benign biocides which have long been used to control decay fungi and insects. However, borates are water soluble and easily leached from wood exposed outdoors unlike waterborne CCA which fixes to wood. Thus, borate systems currently cannot be used in exterior applications and were not discussed. It is possible to form borate complexes with reduced water solubility, but these compounds also have been found to have greatly reduced bioactivity. Several news releases by companies who do not have a history in wood preservation have recently claimed to have developed technology that fixes borates into wood for outdoor exposure applications, but these assertions have not yet been verified. However, basic research by various laboratories has suggested applications or processes by which it might be possible to have borates with reduced leaching potential

while retaining good efficacy. At least one traditional wood protection company is studying a process that may achieve this elusive goal.

We mentioned in the Introduction that the heartwood of certain trees have good durability. In the long-term, molecular technology may be employed to enhance the natural durability of the wood in certain trees.

While wood preservation faces many challenges, we are excited about the future and see wood making an increasing important contribution to benefit humanity. However, this will require long-term and basic studies by many different groups, and any product developed must have sufficient biological and physical properties to satisfy the increasing demands of consumers and a suitable profit margin to justify the necessary R&D efforts.

## REFERENCES

- [1] Goodell B, Qian Y, Jellison J. In: Development of commercial wood preservatives: Efficacy, Environmental, and Health Issues. Am. Chem. Soc. Symp. Series 982, Washington, DC, 2008; Chp. 2.
- [2] Amburgey TA. Development of commercial wood preservatives: Efficacy, Environmental, and Health Issues. Am. Chem. Soc. Symp. Series 982, Washington, DC, 2008; Chp. 3.
- [3] Distel DL. In: Wood deterioration and preservation: advances in our changing world. Am Chem Soc Symp Series 845, Washington, DC. 2003; Chp. 14.
- [4] Craig, SM. In: Wood deterioration and preservation: advances in our changing world. Am Chem Soc Symp Series 845, Washington, DC. 2003; Chp. 15.
- [5] Schultz TP, Nicholas DD, Preston AF. A brief review of the past, present and future of wood preservation. Pest Manag Sci 2007; 63: 784-88.
- [6] Barnes HM. In: Development of commercial wood preservatives: efficacy, environmental, and health issues. Am Chem Soc Symp Series 982, Washington, DC, 2008; Chp. 35.
- [7] Preston A, Jin L. In: Development of commercial wood preservatives: efficacy, environmental, and health issues. Am. Chem. Soc. Symp. Series 982, Washington, DC, 2008; Chp. 36.
- [8] Leithoff H, Blancquaert P, van der Flass M, Valcke, A. IN: Development of commercial wood preservatives: efficacy, environmental, and health issues. Am Chem Soc Symp Series 982, Washington, DC, 2008; Chp. 34.
- [9] Preston AF. Wood preservation: trends of today that will influence the industry tomorrow. Forest Prod J 2000; 50(9): 12-19.
- [10] Preston AF. In: Wood deterioration and preservation: advances in our changing world. Am Chem Soc Symp Series 845, Washington, DC. 2003; Chp. 22.
- [11] Helmer DB. In: Development of commercial wood preservatives: efficacy, environmental, and health issues. Am Chem Soc Symp Series 982, Washington, DC, 2008; Chp. 23.
- [12] Freeman MH, Shupe TF, Vlosky RP, Barnes HM. Past, present, and future of the wood preservation industry. Forest Prod J 2003; 53: 8-15.
- [13] Reisch MS. All Hands on Deck. Chem & Eng News 2004; 9: 14-16.
- [14] Townsend T, Dubey B, Solo-Gabriele H. In: Development of commercial wood preservatives: efficacy, environmental, and health issues. Am Chem Soc Symp Series 982, Washington, DC, 2008; Chp. 33.
- [15] Englot C. In: Environmental impacts of treated wood. crc/taylor and francis, NY, 2006, Chp. 17.
- [16] Saxe JK, Wannamaker EJ, Conclin SW, Shupe TF, Beck BD. evaluating landfill disposal of chromated copper arsenate (cca) treated wood and potential effects on groundwater: evidence from florida. Chemosphere 2007; 66: 496-504.
- [17] Dube E. assessment of potential health risks from cca-treated utility pole. Proc Ann Meet Am Wood Preservers' Assoc 2003; 99: 39-50.
- [18] Freeman MH, Nicholas DD, Schultz TP. In: Environmental impacts of treated wood. CRC/Taylor and Francis, NY, 2006, Chp. 2.

- [19] Kamdem, DP. In: Development of commercial wood preservatives: efficacy, environmental, and health issues. Am Chem Soc Symp Series 982, Washington, DC, 2008; Chp. 25.
- [20] Nicholas, DD, Schultz, TP. IN: wood preservation in the '90's and beyond. Forest Prod Soc, Madison, WI, 1995, pp. 169-173.
- [21] Laks, PE. In: development of commercial wood preservatives: efficacy, environmental, and health issues. Am Chem Soc Symp Series 982, Washington, DC, 2007; Chp. 13.
- [22] Henderson, G. In: Development of commercial wood preservatives: efficacy, environmental, and health issues. Am Chem Soc Symp Series 982, Washington, DC, 2008; Chp. 14.
- [23] Wallace, DF, Cook, SR, Dickinson, DJ. In: Development of commercial wood preservatives: efficacy, environmental, and health issues. Am Chem Soc Symp Series 982, Washington, DC, 2008; Chp. 18.
- [24] 2007 AWPA Book of Standards, Am Wood Preservers; Assoc, Birmingham, AL, 2007.
- [25] Rowell, RM. Chemical Modification of wood: A Short Review. Wood Mater Sci & Engin, 2006; 1:29-33.
- [26] Homan, WJ. In: Development of commercial wood preservatives: efficacy, environmental, and health issues. Am Chem Soc Symp Series 982, Washington, DC, 2008; Chp. 19.
- [27] Lande, S, Eikenes, M, Westin, M, Schneider, MH. In: Development of commercial wood preservatives: efficacy, environmental, and health issues. Am Chem Soc Symp Series 982, Washington, DC, 2008; Chp. 20.
- [28] Militz H. In: Development of commercial wood preservatives: efficacy, environmental, and health issues. Am Chem Soc Symp Series 982, Washington, DC, 2008; Chp. 22.
- [29] Krause A, Wepner F, Xie Y, Militz H. In: Development of commercial wood preservatives: Efficacy, Environmental, and Health Issues. Am Chem Soc Symp Series 982, Washington, DC, 2008; Chp. 21.
- [30] Evans PD. In: Development of commercial wood preservatives: efficacy, environmental, and health issues. Am Chem Soc Symp Series 982, Washington, DC, 2008; Chp. 5.
- [31] Goswami, J.C., Liu, J.-L., Doyle, A.K.: US5925424 (1999).
- [32] Goswami, J.C., Liu, J.-L., Doyle, A.K.: US20016312774 (2001).
- [33] Nicholas DD, Freeman, MH. PXTS: A new environmentally friendly metal free oligomer wood preserving system. Wood Protection, Barnes HM, ed. Proceed no. 7229, Forest Products Society, Madison, WI. 2006; 311-317
- [34] Schultz TP, Nicholas, DD. Wood preservation in the '90's and beyond. Forest Prod Soc, Madison, WI, 1995; 187-193.
- [35] Kumagaya, H.: JP11269014 (1999).
- [36] Pillay, A.S.: US20006110950 (2000).
- [37] Ross, A.S., Marks, B., Ward, H.: US20067056919 (2006).
- [38] Hsu, J.C.: US5591760 (1997).
- [39] Hsu, J.C.: US5759786 (1998).
- [40] Gaffney, T.W., Wiatr, C.L.: US20006069142 (2000).
- [41] Winkowski, K., Tsao, T.: US20006121198 (2000).
- [42] Rustenburg, G., Klaver, C.J.: US20026423732 (2002).
- [43] Kovacevic, S.: US20016262097 (2001).
- [44] Matsugaki, Y., Yamono, T.: JP11286404 (1999).
- [45] Uhr, Buschhaus, H.-U., Kugler, M., Kunisch, F.: US20046828275 (2004).
- [46] Green III F., Schultz, T.P. 2003. IN: wood deterioration and preservation: advances in our changing world. Am. Chem. Soc. Symp. Series 845, Washington, DC. 2003; Chp. 23.
- [47] Ashmore, J.W., Laganella, D.M.: CA147191011 (2007).
- [48] Shoshany, H., Shoshani, A.: US20056908677 (2005).
- [49] Tseng, C.-I., Walker, L.E.: US20036527981 (2003).
- [50] Jiang, X, Walker, L. Amine Oxides for Use in Wood Protection: I. A. Formulation Adjuvant and Performance Enhancer for Wood. Inter Res Group on Wood Protection 2007, paper 07-30425.
- [51] Walker, L.E.: US20036527288 (2003).
- [52] Ward, H.A., Scott, C.C.A.: 14628939 (2005).
- [53] Marks, B., Ross, A.S., Ward, H.A.: US20026416789 (2002).
- [54] Schultz TP, Nicholas DD. Development of environmentally-benign wood preservatives based on the combination of organic biocides with antioxidants and metal chelators. Phytochemistry 2002; 61: 555-560.
- [55] Schultz TP, Nicholas DD, Henry WP, *et al.* Review of laboratory and outdoor exposure efficacy results of organic biocide: antioxidant combinations, an initial economic analysis and discussion of a proposed mechanism. Wood Fiber Sci 2005; 37: 175-84.
- [56] Schultz TP, Nicholas DD. Naturally durable heartwood: evidence for a proposed dual defensive function of the extractives. Phytochemistry 2000; 54:47-52.
- [57] Schultz, T.P., Nicholas, D.D.: US20016231651 (2001).
- [58] Schultz TP, Nicholas DD, Kirker GT, Prewitt ML, Diehl SV. Effect of the antioxidant bht on reducing depletion of chlorothalonil in treated wood after 54 months of ground-contact exposure. Internat Biodet Biodeg 2006; 57:45-50.
- [59] Schultz TP, Nicholas DD. Wood Protection 2006, Forest Prod Soc Madison WI. 2007; 289-94.
- [60] Schultz TP, Nicholas DD, Ingram LL Jr. Laboratory and outdoor water repellency and dimensional stability of southern pine sapwood treated with a waterborne water repellent made from resin acids. Holzforschung 2007; 61: 317-322.
- [61] Schultz, T.P., Nicholas, D.D., Kelley, S.S.: CA147379841 (2007).
- [62] Higaki, M.: US20036527982 (2003).
- [63] Ellis JR, Jayachandran K, Nicholas D. Silver - The next generation wood preservative. Inter Res Group on Wood Protection 2007; paper 07-30419.
- [64] Boettcher, H., Haufe, H., Henker, P., Mahtig, B., Risse, G.: CA147408307 (2007).
- [65] Thys, A.P.M., Bosselaers, J.P.H., Bylemans, D.L.J.: CA147337696 (2007).
- [66] Narayanan, K.S., Winkowski, K., Patel, J.: US2006105007 (2006).
- [67] Stockel, R.F.: US20067074459 (2006).
- [68] Nyssen, P.-R., Spetmann, P.: US20026494941 (2002).
- [69] Narayanan, K.S., Jon, D., Ianneillo, R.M., Prettypaul, D.: US20016251416 (2001).
- [70] Matsunaga H, Kiguchi M, Evans P. Micro-distribution of metals in wood treated with a nano-copper wood preservative. Inter Res Group on Wood Protection 2007, paper 07-40360.
- [71] Hodge, R.L., Richardson, H.W.: US7238654 (2007).
- [72] Richardson, H.W., Hodge, R.L.: CA14258315 (2004).
- [73] Zhang, J., Leach, R.M.: CA147279490 (2007).
- [74] Leach, R.M., Zhang, J.: CA143417591 (2005).
- [75] Richardson, H.W., Hodge, R.L.: CA144371824 (2006).
- [76] Ashmore, J.W., Ghosh, T., Lasas, J.P.: CA154440095 (2006).
- [77] Laks, P., Heiden, P.A.: US6753035 (2004).
- [78] Liu, Y., Laks P, Heiden, P. Nanoparticles for the controlled release of fungicides in wood: soil jar studies using g. trabeum and T. versicolor. Holzforschung 2003; 57:135-139.
- [79] Liu Y, Laks P, Heiden, P. Controlled release of biocides in solid wood: iii. preparation and characterization of surfactant-free nanoparticles. J Appl Polym Sci 2002; 86:615-621.
- [80] Watkins, J.B., Greaves, H., Chin, C.W.: US5098472 (1992).
- [81] Watkins, J.B.: US20036503306 (2003).
- [82] Crawford DM, De Groot RC. Treatability of u.s. wood species with pigment-emulsified creosote. Forest Prod J 2000; 50(1): 29-35.