

CARBON BASED WOOD PRESERVATIVES: APPLICATIONS AND NEW OPPORTUNITIES

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Summary

The use of non-metal, carbon based compounds to protect wood is increasing. There are a number of compounds that are useful for protecting wood from degradation by insects and decay fungi. The characteristics and attributes of the different carbon based preservatives are well suited to provide long term wood protection. Current and future advances are utilizing synergistic active ingredient combinations, sophisticated delivery systems and stabilization and protection strategies to deliver optimal performance.

Introduction

Wood can be degraded by both biotic and abiotic factors. Short term degradation of fresh sawn lumber, referred to as sapstain or blue stain, is caused by fungi. Fungi are also responsible for surface mould and for wood decay. The organisms are quite different for each type of degradation as are the strategies for protecting the wood. Wood can be attacked by insects such as termites and wood borers as well. Abiotic degradation of wood can be by checking and cracking due to moisture induced dimensional instability, by ultraviolet light degradation and by fire. This paper will focus on the use of carbon based preservatives for protection against the biotic degradants.

Early Carbon Based Preservatives

For centuries metal salts have been known to protect wood from decay but were not utilized to any great extent due to the preference for durable species and abundant forests. The use of coal tars and eventually creosote is likely the first commercial wood treating system (Barnes, 2008). Distillation of coal tars to creosote and developing treatment processes occurred in the late 1800's. Today creosote remains in widespread use for rail ties, utility poles and pilings, but, not for residential use. Creosote is a complex mixture of polycyclic aromatic hydrocarbons, phenols and creosols. (USEPA, 2008)

In the 1930's phenolic compounds, particularly pentachlorophenol, were utilized commercially for protecting wood from fungi and insects (Ibach, 1999). Pentachlorophenol is traditionally incorporated into oil based carriers and then used to impregnate wood, providing long term protection of, for example, utility poles in ground contact. Incorporating pentachlorophenol in lighter organic solvents such as mineral spirits was used for dip treating millwork.

Pentachlorophenol was also used to protect fresh sawn lumber from staining fungi by surface spray or dip application. Pentachlorophenol remains in use today primarily for preserving utility poles.

Current Carbon Based Preservative Compounds

There is a diverse but limited selection of carbon based preservative compounds available for developing treating formulations. The compounds are suitable for protecting against stain, molds, decay and soft rot and can be used for temporary protection or for longer term aboveground and ground contact decay protection.

Quaternary ammonium compounds are approved for wood protection uses for temporary protection of sapstain and mold organisms and also for aboveground protection from decay. Quaternary ammonium compounds are comprised of a positively charged nitrogen covalently bonded to two methyl groups and to two alkyl groups of varying lengths, but having one with at least eight carbons. As cationic surfactant type active substances they interact with phospholipid-bilayer structures, severely alter the cell wall permeability, disturb membrane-bound ion-translocation mechanisms, and may facilitate the uptake of other biocides (CIRCA, 2007). The compounds are salts of either bromine or chlorine. Quaternary ammonium compounds are approved in the US and Canada for use on wood (USEPA, 2006) and are being supported and the evaluations are ongoing through the Biocides Product Directive (BPD) approval process in Europe for use as wood preservatives (Leithoff, 2009).

3-iodo-2-propynyl butyl carbamate (IPBC) is a widely used wood preserving compound. The mode of action of this molecule is still unclear, however, it is hypothesized that the fungicidal property is caused mainly by the terminal iodine (Jürgensen et al., 2000). Others propose that carbamates disturb the acetylcholine esterase activity (Jarrad et al., 2004) or interact with the cell membrane permeability (FRAC, 2007). The compound is used for protecting wood from sapstain and mold as well as for decay control for aboveground exposures. IPBC is also used in coatings applications for surface mold protection. IPBC is approved for use on wood in the US and Canada and has been accepted by the BPD for use as a wood treatment (Troy Chemical Corporation, 2006).

The triazoles are a group of highly active antifungal compounds with varying chemical structures and spectra of activity. The common moiety of the triazole is a five-member ring with three nitrogen atoms. Their primary mode of action is by interfering with the fungal metabolic systems, typically ergosterol biosynthesis (Buchenauer, 1987). Azaconazole was one of the first triazoles developed for wood protection and it had specific activity against sapstain (Wakeling *et al.*, 1995). Propiconazole protects wood from both stain and decay organisms whereas tebuconazole and cyproconazole are specifically active against decay (Buschhaus and Valcke, 1995). Azaconazole was registered in Canada for wood protection, but subsequently discontinued. Propiconazole is registered in the US and Canada for sapstain and decay and has been accepted under BPD for use on wood. Tebuconazole is currently registered in the US and

Canada for wood decay control and has been accepted under BPD for wood protection in the EU. (Leithoff, 2009)

TCMTB (1,3-benzothiazol-2-ylsulfanylmethyl thiocyanate) is used for the control of sapstain organisms on wood in both the US and Canada (USEPA, 2006). Fernandez-Alba et. al. (2002) implicate the inhibition of mitochondrial electron transport as the mode of action. This compound has not been supported as a wood preservative under the BPD regulation.

MBT (2-mercaptobenzothiazole) is active against stain and mold organisms on wood. Czechowski and Rossmore (1981) propose the inhibition of lactose dehydrogenase and the complexation of divalent ions as possible mode of action. It is approved for use on wood in the US and Canada (USEPA, 1994), but has not been defended for this use under BPD.

Chlorothalonil (tetrachloroisophthalonitrile) is a compound with a chemical structure very similar to that of pentachlorophenol. It is comprised of a six member ring, four of the carbons in the ring have an attached chlorine atom, the other two are terminated with a carbon triple bond nitrogen. The postulated mode of action is the conjugation with, and depletion of thiols (particularly glutathione) from germinating fungal cells, leading to disruption of glycolysis and energy production (e-Pesticide Manual, 2003). This compound is active against mould, sapstain and decay and is approved for use as a wood preservative in both the US and Canada (USEPA, 1999). It has not been supported under the BPD.

Isothiazolone, specifically 4,5-dichloro-2-n-octyl-3(2H)-isothiazolone (DCOI) recently received approval for use as a wood preservative in the US. A multi site mode of action is assumed for this molecule, however, it interacts especially with essential enzymes containing thiol groups, and effects membrane permeability and nucleic acids (Sox, 1997). The compound is active against mould and decay in aboveground exposure applications. (Chapman *et. al.*, 2000) It is approved for non-wood uses in Canada and is being evaluated as a wood preservative under the BPD.

PXTS is an oligomeric mixture of alkylphenol polysulfides formed by reacting cresylic acid with sulfur chloride and sulfur (mode of action unknown to the author). PXTS is registered for wood protection in the US and approved for use in ground contact applications by the AWPA. PXTS is active against decay, soft rot and termites. (Goswami, *et. al.*, 1999) It is not registered in Canada and is not submitted for BPD approval.

Thiabendazole is a benzimidazole compound with specific activity against surface molds (Clausen and Yang, 2003). Thiabendazole interferes with the β -tubulin assembly in mitosis (FRAC, 2009). In the US it is approved for incorporation into paint and wood stains. In Canada it is registered for non-wood uses. It has been accepted for application to wood under the BPD.

A limited number of carbon based termiticide compounds are available. In the past, chlorpyrifos (cholinesterase inhibitor) was used, however many of the uses for this compound, including wood, have been withdrawn. The pyrethroids (act on the nervous system / the function of

neurons of the insect by interaction with the sodium channel) are synthetic analogs of the naturally derived pyrethrin insecticide. The two synthetic pyrethroids currently available for wood protection are permethrin and bifenthrin (Obanda *et. al.*, 2007). Both are registered for use on wood in the US and both are being evaluated by the BPD. Imidacloprid and thiamethoxam are neonicotinoid compounds (antagonists, binding to nicotinic receptors in the insect central nervous system) with termiticidal activity. They are approved for use on wood in the US. Thiamethoxam is being defended under BPD but imidacloprid is not. (e-Pesticide Manual, 2003)

Market Factors

There is a prevailing mind set in the North American wood industry, that is, that wood is a commodity and that therefore the typical laws of supply and demand go into effect. The greater the supply of wood, the lower the price, and vice versa. The same perception is carried over treated wood. But this commoditization of the treated wood product ignores the value added by the wood treatment chemicals and their development costs, and negates the value of the application process. Consumers send mixed messages about their expectations for treated wood and the associated value. They do not have enough information to differentiate between different treatments and the treated wood properties. (Vlosky and Shupe, 2005)

The source of many of the carbon based preservatives are compounds that have been developed and registered for use in agricultural crop protection (Helmer, 2006). While this strategy brings a broader range of carbon based wood preservatives than might be supported by the wood protection use alone, it leaves them vulnerable and dependant on the continuation of their use in agriculture. If for example a compound was no longer supported for agricultural use, the wood protection application could feasibly no longer be defended as well.

The costs to manufacture the carbon based preservatives remains fairly constant based on the starting materials and the energy needed to produce them. Typically, the greater the production volume, the lower the cost per unit produced. The carbon based preservatives compete against the non-carbon based preservatives like, for example, copper. In March 2005 the price of copper was about \$1.50 per pound. Copper based treatments for wood were quite inexpensive and the interest and demand for carbon based preservatives was low. By August 2007 the copper price was about \$3.80 per pound and as a result, the demand for carbon based preservative alternatives was very high. In January 2009, copper prices were back below \$1.50 per pound. From a business development perspective, this is a very difficult situation to deal with.

Biotic and Abiotic Factors

Traditional active substances with a broad spectrum of efficacy were used as a single active ingredient or in combination with a second active ingredient at a high dose to cover the whole broad spectrum of wood damaging organisms. Carbon based preservatives are selected because

of their high degree of specific activity. As a result, they are used against select organisms and are effective at relatively low doses. In combination with other actives they lead to a coverage of the full spectrum at an in total lower retention of the wood preservative and allow to develop cost effective wood preservatives.

The preservative delivery system is very important to the efficacy of the treatment. The treatment formulation can impact distribution of the active substances or the stability in solution. Typically the carbon based preservatives have relatively low water solubility so emulsion and micro-emulsion techniques are employed to deliver the preservative into the wood (Preston, 2004). However, solid carbon based actives may also be applied in a micronized form as this was introduced for copper recently (e.g. McIntyre et al., 2009). It might be noteworthy that in case of carbon based insecticides the distribution within the cell wall can be neglected as the insects / respectively their larvae consume the wood fibers or parts of them as a whole.

Carbon based preservatives are degradable and biodegradable. This is both a strength and a weakness. The lessons of persistent biocides have been learned, but the expectation that a preservative will offer an extended service life to a piece of wood places a high demand on stabilizing a degradable compound in the treated timber for the desired period of service.

Wood preservatives leach out of wood. Exposure of outdoor wood to water is unavoidable. Because of the inherent low doses of the carbon based preservatives, and the high performance standard, the depletion of even small amounts of active ingredient can significantly impact the long term performance of a carbon based preservative system. Traditionally these expected losses could be compensated for by applying actives in excess in the treatment this practice will likely be limited in the future due to regulations addressing the impact of biocide emission to the environment and by economic pressure. Therefore, in the future formulation technology and depletion mitigating measures that limit the emission of actives will gain importance.

Current Uses for Carbon Based Preservatives

Carbon based wood preservatives have approval for use in a variety of wood products today including short term protection of fresh sawn lumber from sapstain and mould, or for mould control on, for example, pallets. Engineered wood products are pressure impregnated for protection against termites and decay. Millwork, window and doors for outdoor exposure are typically coated, but treated with preservatives for protection against decay and termites. Outdoor treated wood for out of ground contact uses includes decking, highway sound barriers, outdoor buildings, shingles and shakes, siding, and trim boards. Carbon based preservatives for decay and termite protection are used in remedial treatment applications. (Schultz *et. al.*, 2008.)

Carbon based wood preservatives are typically used in combination with other wood preservatives. Since in today's climate, the goal is not necessarily to have a completely metal free preservative system (unless the metals become astronomically expensive), carbon based preservative s are combined with, for example, copper. The idea is to provide some insurance in

the event of exposure of the treated wood to decay fungi that are copper tolerant. But carbon based systems are developed, for example, in sapstain control in order to protect against a broad range of potentially damaging organisms and to take advantage of the specific strengths of the different preservative components (Schauwecker and Morrell, 2008).

Strategies Moving Forward

The most obvious challenge and area of interest is to find new active ingredients that have unique activity or are more cost effective or that are somehow more competitive with the current wood preservatives in commerce today. Certainly many companies are screening candidates every day. The reduced numbers of new active ingredients being introduced into the agricultural sector gives an indication that this avenue is not as promising as in the past.

Probably the most activity is underway to explore the development of new products and delivery systems with the arsenal of active ingredients at hand. Screening combinations and ratios in laboratory and field trials represents a significant portion of the wood preservative development activities being conducted today.

In the course of screening these combinations and ratios of active ingredients, there is always the anticipation of identifying a synergistic combination where the level of observed activity is greater sum of its components' individual activity. These synergies are patentable and can make a significant contribution to a competitive position in the market.

Adjuvants are substances that are added to formulations but that have no activity on their own. These additives may impart some characteristics that enable the active ingredients to perform better (Helmer, 2006). The intent is to identify an inexpensive performance booster offering a commercial advantage to the treatment system.

The use of antioxidants in combination with carbon based preservatives has been well described and holds promise to improve the long term performance of carbon based preservative systems (Schultz, *et. al.*, 2007). Their hypothesis is that these antioxidants scavenge the free radicals utilized by the decay fungi to degrade wood.

The use of water repellants to protect wood is common practice. Adding a water repellant to wood treatment system, protects the preservative from the effects of moisture for a limited time. Furthermore, this earl protection extends the effective preservative life by more than just the initial time afforded by the water repellant. An explanation given by Zahora (2000) is that the water repellant enables the preservative to have more time to bind itself to the wood and thus ultimately resist effects of moisture more effectively.

It has been reported that bacteria can attack and degrade wood preservatives in the soil (Wallace and Dickinson, 2004). By using biocides active against these bacteria offers the possibility to

slow down the rate of preservative degradation and thus increase the service life of the treated wood.

Physical and chemical wood modification techniques have shown promise for increasing the durability of wood. Furfurylation, acetylation and thermal treatments are in various stages of commercial development. These modifications impart some measure of decay resistance, but, often focus to improve the mechanical properties and the stability of the wood. (Van Acker, *et al*, 2004) By combining a low dose carbon based preservative with a thermal or chemical treatment, a durable and stable piece of wood with long term decay protection could be achieved.

Barrier wraps for ground contact applications have been developed and are gaining some popularity for protecting the below ground portions of, for example, fence posts. The AWPA approvals in place for these today allow the barrier wraps to be used in addition to the traditional ground contact approved treatments. Investigations are underway to determine the potential for long term efficacy of reduced treatment levels combined with barrier wrap applications. (Freeman, *et. al.*, 2005)

Outlook

In the future if some of the challenges described herein can be met, carbon based preservative treated wood could be used for industrial uses like bridge timbers, railroad ties, utility poles or marine bulk heading. Ground contact uses for carbon based preservative systems is feasible if the specific demands of that application can be met.

New treatment systems offer opportunities for new performance levels. In Denmark Superwood is operating a treating plant using supercritical fluids to apply carbon based preservatives, thereby eliminating water and waste treating solution. Kop-Coat, Inc. has the True Core treating system that shows promise for improved preservative penetration.

New formulation technology platforms that improve penetration and deposition within the wood would be welcomed by the industry. Formulations that offer improved protection of the active ingredients in service from both biotic and abiotic degradation are needed. Ultimately formulations with enhanced preservative performance characteristics are needed. Finally, the search for new carbon based active ingredients could bring these preservatives into a wider acceptance and utilization.

Carbon based preservatives have gained a degree of acceptance, but innovations are needed for them to be suitable for use in the more heavy duty use categories.

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