New approaches to wood protection

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Introduction

In the United States, billions of dollars are spent annually to replace wood damaged by decay fungi or infested with termites. Equally costly are the insurance claims for mould clean up in houses. All three wood inhabiting organisms are attracted to excess moisture. Realistically, moisture control is undermined by a combination of factors including architectural style, workmanship, building materials, building practices, weather, energy efficiency, and maintenance. Protection of wood from biological agents is also achieved by preservative treatments with biocides. Since chromated copper arsenate (CCA)-treated wood was restricted from most residential applications in the U.S. the need for new "green" wood protection systems has increased. Several environmentally friendly approaches to heavy metal-free wood protection are being investigated including targeted biocides, synergistic combinations of new and existing biocides, nanotechnology, and naturally durable wood species. Developments in each area will be discussed.

Heavy metal-free technologies

Targeted biocides

Chemicals to protect wood from biodeterioration by fungi and termites have generally been broad-spectrum biocides that are now facing increasing environmental regulatory pressure. A more logical approach to development of selective biocides would be to define a target, characterize that target, and then design inhibitors based on the mechanism of action of the defined target. Targeted biocides may act by sabotaging the mechanism of fungal infection or disguising

structural components of wood from fungal recognition. One targeted biocide developed and patented is N, N naphthaolylhydroxyamine (NHA), a low toxicity, water soluble, calcium-precipitating stain typically utilized in electron microscopy. NHA forms a stable calcium precipitate in calcium containing wood cell wall structures such as the bordered pit membrane and compound middle lamella. Fungal infection is halted to two ways; first, by altering the path for hyphal movement from cell to cell and second, by interference with metabolism of decay fungi. NHA is also a direct termiticide and at low concentrations, it acts as a feeding stimulant resulting in termites consuming twice as much of a commercial termiticide, often a chitin synthetase inhibitor, in cellulose termite bait systems.

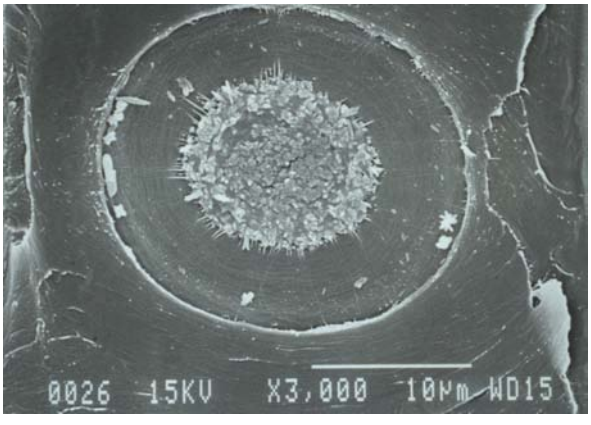

Figure 1. N, N naphthaolylhydroxyamine alters the pathway for fungal infection by forming a stable calcium-precipitate on the bordered pit membrane.

Essential oils

Essential oils from herbaceous plants, used most often in the food industry as flavoring, the cosmetics industry as fragrance, and the pharmaceutical industry for their functional properties, are now being evaluated as fungitoxic and insecticidal wood protectants. Their naturally occurring anti-microbial properties are conferred by monoterpenes, diterpenes and hydrocarbons with various functional groups. Primary chemical constituents of essential oils vary considerably between oils. However, AFNOR (Association French Normalization Organization Regulation) and ISO (International Standards Organization) certification standardizes the chemical profile and principal constituents that differentiate thera-

peutic grade from lower Grade A essential oils ensuring a minimum levels of activity is present for a specific oil. Selected herbaceous plant essential oils have demonstrated high efficacy towards mould fungi, decay fungi, and termites. Our research has shown that dill weed oil selectively acts as a fumigant to cause 24-hr mortality to subterranean termites. Egyptian geranium and white thyme oils selectively inhibit mould and decay fungi when used as a surface treated for wood suggesting they may be useful for inhibition of mold fungi on wood and wood products in service. The volatile components of dill weed oil are better suited as fumigants for protection of stored building materials, such as framing lumber, millwork, or truss systems.

Fatty acid chemistry

Fatty acids, used successfully as agricultural fungicides, are being evaluated for antifungal activity against the wide variety of ascomycetes, deuteromycetes and basidiomycetes inhabiting wood. Conditions affecting the efficacy of fatty acids on wood products need to be identified. Previous research, though scant, suggests that fatty acids demonstrate a high degree of specificity towards inhibition of spore germination of brown- and white-rot basidiomycetes that is dependant on the fatty acid, concentration tested and the test organism. Fatty acid formulations require an emulsifier to form a miscible dispersion; some emulsifiers possess some degree of antimicrobial activity and can be used to selectively enhance efficacy of a fatty acid formulation. Adjuvants, such as organic acids, may be useful to further enhance the performance of fatty acids. Many organic acids are classified as GRAS (Generally Accepted As Safe) compounds by the U.S. Food and Drug Administration (FDA) and have common acceptance for use in the food industry as acidulants and flavor enhancers. The safety record of these compounds is a positive feature for development of antimicrobial formulations based on “green chemistries”. Adding organic acids, such as L-lactic acid, to the fatty acid emulsifications may increase the proportion of non-ionized fatty acids over ionized species, thereby promoting greater fatty acid penetration through cell membranes. Intracellular proton pump activity is increased and more energy is required by the cell for electrolyte balance, thus placing more stress on the cell. Higher intracellular concentrations of free fatty acids possibly results in damage to organelle membranes and protein structure. Multifactorial fatty acid emulsifications incorporating an appropriate adjuvant are promising for effective protection against numerous fungal species that affect wood products. Using this

strategy, new “green” wood protection formulations are being developed and their application is likely to extend to other biodeteriorating agents such as termites and decay fungi.

Synergistic biocide combination

Finding a single, synthetic or natural antimicrobial compound, either newly recognized or already registered, to inhibit the immense variety of fungi capable of colonizing wood and wood products is highly unlikely. Likewise, biocide resistance that occurs frequently and to varying degrees in wood-inhabiting fungi increases the importance of co-biocide interaction for successful wood protection. Synergistic combinations of selected compounds, preferably using those derived from natural sources, is generally recognized as the most promising approach for obtaining successful control of wood inhabiting organisms. A synergistic biocide for interior application, called Durazol, has been developed based on several components that are well known to the wood preservation industry, namely boric acid, propionic acid and quaternary amine compound. While the preservation industry is also familiar with two azoles, propiconazole and tebuconazole, Durazol incorporates thiabendazole as a mould inhibitor. Thiabendazole is an agricultural fungicide that has greater efficacy towards mould fungi than either propiconazole or tebuconazole. The combination of actives in Durazol act synergistically to protect wood from a number of test fungi and termites at lower concentrations than are required for individual active ingredients.

Nanotechnology

Nanotechnology has the potential to greatly impact the wood protection industry through the creation of nanobiocides and nanomaterials with unique properties. Two areas of nanotechnology are currently being investigated, nanometals and nanocarriers.

Nanometals

Nanobiocides may find applications as co-biocides, or may alter treatability properties such as penetration and biocide distribution. Nanometals typically used by the wood preservation industry, namely nanocopper oxide and nanozinc

oxide, were evaluated for leachability and efficacy of treated southern pine against mould fungi, decay fungi, and subterranean termites. Nanocopper and nanozinc showed favorable leach resistance compared to their soluble metal oxides. Nanozinc also inhibited termite feeding and caused moderate termite mortality. Both nanozinc and nanocopper inhibited a white-rot test fungus and were approximately as effective as their soluble counterparts at inhibiting brown-rot test fungi. Neither was effective against mould test fungi.

Nanocarriers

Nanotubules made from ceramics, clay, metal or lipids have been used as carriers in various medical and industrial applications. Some properties of nanocarriers that would benefit the field of wood protection include:

- Delivery and placement of biocide
- Slow release of a biocide
- Release of the biocide upon exposure to certain environmental conditions, such as high humidity
- Protection of heat labile organic biocides during treatment processes or panel fabrication.

Nanotubules can be capillary-loaded in a process that is highly dependent on the internal diameter of the nanotubule, chemical viscosity and solubility as well as chemical reactivity to the nanotubule material. Capillary loading may also rely totally on adsorption of the chemical. Resistance of physical forces is not only important to capillary loading of nanotubules, but is also important in the release of the treatment chemical, both intentional slow-release and unintentional leaching.

Loaded nanotubules may be used for surface application, pressure impregnation, or as an additive to engineered products, films, coatings or sealants. Some considerations include how to precisely control release of a biocide, compatibility with resin if used to treat composites, whether the resin itself may be a barrier to release of the biocide, risk of release during finishing, refinishing, or sanding, as well as calculating and regulating actual release rate. Proper design could lead to increased applications for biocides that are otherwise unsuitable for exterior or in ground applications, including but not limited to soluble biocides, heat labile biocides and delivery of targeted nanobiocides.

Figure 2. Painted gypsum board demonstrates effectiveness of controlled release nano-carrier following challenge with *Aspergillus niger*. Untreated control (left); treated with nanotubules loaded with commercial biocide (center); treated with nanotubules loaded with nanosilver (right).

Naturally durable wood species

The current emphasis on green technologies has renewed research interest in utilization of naturally durable wood species. Extractives have long been recognized as key features that impart natural durability in the heartwood of certain wood species. Extractives from some wood species have been evaluated for use as environmentally friendly preservatives or additives to coatings, but little is known about the chemical makeup of the extractives from underutilized wood species. In the U.S. there is also a need to find new uses for invasive and low-value, underutilized wood species in order to reduce the fire fuel load and restore the health of our National forests. Invasive and underutilized wood species selected for their natural durability are being evaluated in aboveground simulated deck tests in different decay hazard zones. Concurrently, bioactive extractives are being characterized in the laboratory. Successional microbial changes are being determined with T-RFLP and successional changes in chemical extractives are being followed during long-term outdoor exposure. Bioactive extractives responsible for imparting durability could provide new environmentally benign wood protection systems for aboveground applications.

Figure 3. Naturally durable underutilized and invasive wood species in aboveground simulated deck test.

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VTT SYMPOSIUM 263

Keywords: biomaterial, wood, fiber, composite, packaging, passive building

2009 Wood and Fiber Product Seminar

VTT and USDA Joint Activity

September 22–23, 2009

Edited by

Ali Harlin & Minna Vikman

Organised by

VTT

ISBN 978-951-38-7589-3 (soft back ed.)
ISSN 0357–9387 (soft back ed.)

ISBN 978-951-38-7590-9 (URL: http://www.vtt.fi/publications/index.jsp)
ISSN 1455–0873 (URL: http://www.vtt.fi/publications/index.jsp)

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puh. vaihde 020 722 111, faksi 020 722 4374

VTT, Bergsmansvägen 5, PB 1000, 02044 VTT
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Edita Prima Oy, Helsinki 2010