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Wood preservation using natural products

Preservación de la madera usando productos naturales

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ABSTRACT
It is a current concern in the wood preservation field to avoid the use of toxic chemicals and develop new technologies based on low environmental impact agents and sustainable principles. Under this expectation, an intended state-of-the-art is introduced on the application of natural products such as traditional tar and wood oils as well as tannins and plant extracts. A particular revision to heartwood chemical components is offered. The combined methods of using natural and chemical components are reviewed, considering as outstanding the mixtures of natural organic constituents with cooper and boron salts that seem to be under encouraging experimentation. Fungicides and anti-termite applications are commented as well the leaching problem of inorganic salts. Chemical modification of wood structure through the formation of adducts and the treatment with nanomaterials are promising tools that will change the actual view and performance of wood preservation techniques.

KEYWORDS: bark, biocides, extract, fungicide, oil, phenolics, tannins, termites.

INTRODUCTION
Wood as a natural renewable resource plays an important role in the world economy, particularly in the construction and furniture fields. The expectation for better options in preserving wood from biodegradation during storage, transportation, manufacturing, and in service is actual. Environmental issues from the conventional toxic chemical preservatives containing metals for wood treatment and their disposal problems have urged the search for more ecologically friendly technologies. The current progress and implementation of new technologies has been limited due to variability between the laboratory and the field performances of natural products alternatives, and legal problems derived from the lack of globally
defined quality standards. Plant extracts, biological control agents, and combination of chemical and natural processes are emerging as partial solutions to control wood deteriorating organisms such as fungi, bacteria and termites.

Any wood protection plan may involve a systematic approach, starting with moisture control as most wood attacking organisms require a water source. Finishes, including water repellents, can help to protect wood in slight deterioration environments, as above ground conditions. Durable wood, including heartwood from naturally resistant species and chemically treated wood, can be used to replace deteriorated wood in moderate to extreme locations such as ground contact (Loferski, 1999).

Since a previous review on tannins as wood protection agents (González-Laredo, 1996) some important advances have been made in the exploration of new organic and natural biocides for the development and innovation of sustainable processes to be applied for wood preservation. Since then several interesting reviews have been published (Singh and Singh, 2012; Verma et al., 2009; Yang, 2009; Mai et al., 2004). Also a dozen of related patents intended to extend service life of wood and wood products using some natural bioactive components have been conceded (USPTO, 2013). It continues to be imperative developing sustainable technologies for protecting wood and wood products from biodegradation with a minimum environmental impact. It is expected that at some point the totally organic systems will be required for wood products in residential uses.

**Natural Durability - Wood Protection from Trees**

The wood protection against biodeterioration is closely linked to the accumulation of extractives typically in the heartwood. They are often produced by the standing tree as defensive compounds to environmental stresses, conferring natural resistance. However, extractive content is highly variable not only from tree to tree but also within an individual tree. Therefore, it is a big challenge trying to standardize these materials and recommend service life spans and performances. These non-structural chemical components play a major role in the susceptibility of wood against wood decay organisms. Using a wide selection of extraction methods, extractives from naturally durable wood species have been used to inhibit a wide range of organisms from human pathogens to insects, wood decay fungi, and mould fungi (Kirker et al., 2013). The attack of these organisms in general can be prevented with synthetic organic and inorganic preservatives. Although most of them are harmful to human health and the environment, it has been shown that it is encouraging the application of wood extractives as natural preservatives.

It is known that the heartwood is the naturally resistant part of tree woods, while sapwood in almost all species has no natural durability. The extractive compounds are produced as the living ray cells in the inner sapwood zone die, forming the non-living heartwood. As the sapwood dies in wood species with durable heartwood, a series of reactions in the storage or parenchyma cells of the wood rays converts the stored sugars and starch into a diverse group of biocides that constitutes the new heartwood chemicals (Scheffer and Morrell, 1998). The leading components of wood extractives are tannins, obtained typically from tree barks; flavonoids, exhibiting antifungal and feeding deterrent activities against subterranean termites (Carrillo-Parra et al., 2011; Reyes-Chilpa et al., 1995; Reyes-Chilpa et al., 1997; Reyes-Chilpa et al., 1998; Sundararaj et al., 2015); quinones, with natural repellent and toxic properties, mainly against termites; and stilbenes imparting natural heartwood durability, mainly for its resistance to fungal (Nascimento et al., 2013).

The role of extractives in durability of eight wood species compared to a nondurable control was evaluated in laboratory for resistance to termite attack and decay by brown-rot and white-rot decay fungi (Kirker et al., 2013). Nearly all of the wood species displayed higher weight loss due to termite or fungi when extractives were removed, which was comparable to the nondurable controls. It has been suggested that micro-distribution of extractives within the wood may be more important than incidence of bulk extractive in the heartwood, although
in-situ studies of extractives are extremely difficult. Both quantity and particularly quality of extractives have a key role, but their relative contribution varies considerably from substrate to substrate. Moreover, Morrell (2011) confirmed in western juniper that the presence of heartwood had no effect on durability of adjacent sapwood. This was observed while testing two Hawaiian heartwoods with exceptionally resistance to termite and fungal attack in non-soil contact, where juniper heartwood was shown slightly less resistant to attack.

Stirling et al. (2007) have evaluated individual components of western red cedar extracts and determined their role as biocidal, metal chelators, or radical scavenger. They found that thujaplicins, β-thujaplicinol, and plicatic acid were toxic to decay fungi and good metal chelators. Plicatic acid and β-thujaplicinol showed also excellent radical scavenging activity. According to Morris and Stirling (2012), some of the protective compounds in the cedars remain under typical field exposure (UV, rain), but are removed through solvent exposure. Thus, leachability of natural wood extractives presents a major obstacle for wood use in ground exposure. Extractive content is primarily responsible but not directed correlated with durability. Therefore, it is probable that individual components of extractives confer durability rather than bulk presence of extractives. An additional factor that may also confer resistance to leaching and decay is the physical barrier from the peculiar wood cell anatomy. It may provide additional protection against fungal colonization or resist any severe extraction from removing the chemicals present in the heartwood.

Bark extract from mimosa (*Acacia mollissima*) and quebracho heartwood extract (*Schinopsis lorentzii*) have shown antifungal resistance, while pine bark (*Pinus brutia*) was ineffective, when tested against white rot fungi and brown rot fungi (Tascioglu et al., 2013). These plant extracts are known for their high condensed tannin contents. When extract retentions in wood samples increased, the resulting mass losses of all tested species decreased. Commercial mimosa and quebracho extracts may be used at concentration levels of 9% - 12% as wood preservatives against common wood decay fungi for indoor applications. Similarly, these extracts have shown termicidal action against *Reticulitermes grasei* at relative high retentions above 90 kg/m³ on pine and 85 kg/m³ for beech samples, suggesting their use as environmentally sound alternatives for wood protection (Tascioglu et al., 2012).

In the tropical rain forest, the pressure from insects and fungi has prompted the development of highly resistant and long living species. As a consequence, some woody plants are appreciated for their resistance to decay, which may be explained by the relatively high levels of extractives, mainly in their heartwood. Such is the case of seven woody species (*Bagassa guianensis, Manilkara huberi, Sextonia rubra, Vouacapoua americana, Andira surinamensis, Handroanthus serratifolius*, and *Qualea rosea*) studied by Rodrigues et al. (2012) with varying natural durability against soft-rot, brown rot, and white rot degradations. From the seven wood extracts, the one from *H. serratifolius* was the most effective even compared with commercial standards.

During heartwood formation, many tree species produce higher quality resistant wood by inserting mainly phenolic substances in the formed cell walls as in the case of black locust (*Robinia pseudoacacia*). This has inspired the modification of wood properties by a chemical treatment with commercially available hydrophobic flavonoids (Ermeydan et al., 2012). Inserting hydrophobic molecules into wood cell walls following a tosylation pretreatment has provided an alternative and well-suited way to significantly reduce the water uptake of cell walls. The resultant artificial heartwood improved its dimensional stability and wood performance applying the basic principles of chemical and physical polymer interactions among the lignocellulose cell wall and simple or polycyclic phenolic compounds.

**Plant extracts**

Traditionally, natural extracts has been explored throughout history to protect wood. Oils, tars and extracts were used to impregnate wood structures, but their availability and economic feasibility have not promoted their exten-
sive use. Steam distillation for oils, water soluble and selective extraction with organic solvents for extracts, and pyrolysis for tars have been the processes used to produce raw wood preservatives. The natural sources have been almost any part of select wooden and herbaceous plants: bark, heartwood, fruit, seeds, and leaves. Among sources of plant oils (either vegetal oils or essential oils), flax seeds (Lyon et al., 2007a), cinnamon (Lin et al., 2007), citrus peels (Macias et al., 2005), and tung seeds have been experimented as potential wood protectors, showing diverse activities as antibacterial, antifungal, antitermite, and antinematode agents. The list continues with exotic sources such as the oil from the nut of kukui plant (Aleurites moluccana), which is being used to protect canoes against marine borer damage according to native folklore (Nakayama and Osbrink, 2010). However the results indicated that this oil acts as a feeding deterrent rather than a toxic agent. Parallel interest has incited to explore the major active components present in such oils and extracts, by example cinnamaldehyde in the case of cinnamon, and turpentine and volatiles in orange peels.

It has thought that toxicity and antioxidant properties of bark extracts such as mangrove plant (Rhizophora apiculata) may impart natural resistance to termite action (Khalil et al., 2009). Dewaxed bark was extracted with methanol and successively partitioned with chloroform, ethyl acetate (EA), and butanol. A chromatographical guided purification by a termite bioassay gave the EA fraction as the more active with a distinctive composition of bioactive constituents based on aromatic carboxylic acids and phenolics. These results suggest that the astringency of polyphenols and their antioxidant activity may play a role in preventing termite attack.

**Oils and Moisture Control**

Controlling moisture content is a very effective way of protecting timber because treating with biodegradable tall oil, reduces the capillary water uptake of pine sapwood. However, there are two problems that limit the extensive use of tall oil for wood protection, the amount of oil needed and its tendency to exude from the wood. The emulsion technique is one way of providing high water-repellence efficiency at low oil retention levels (Hyvönen et al., 2006). This has environmental benefits as it uses water as a thinner, instead of the common organic solvents. Another option is to promote the oxidation and polymerization of the crude tall oil, which can be accelerated by iron catalysts, thus preventing the oil from exuding out of the wood and keeping the water repellent efficiency (Hyvönen et al., 2007a). Limiting to some extent the water uptake by the emulsion technique will allow the tall oil to dry, and promoting the in situ iron oxidation will keep it into the wood (Hyvönen et al., 2007b). This may be performed in one single step in existing wood preservation plants.

Vegetable oils may be potential preservatives when applied as a layer into wood surface by decreasing water absorption and actually performing as water repellents (Tomak and Yıldız, 2012). Still, impregnation with vegetable oils is not enough to impart tolerable biological resistance against decomposition factors (i.e., decay or insect attack), but actually easing wood to burning. In fact the need of high oil absorption level required for good protection make the process impractical. However, the concept can be improved adding biocides and optimizing the retention of oil needed. By example, drying oils are commonly used for preserving solid wood or wood composites in combination of metals to form a copper ammonium acetate complex wood preservative (Roos and Acher, 2004). The preservative is applied effectively into the wood to improve its decay and termite resistance. The drying oil in the wood reduces water absorption and swelling, increasing its mechanical strength; even in a wood composite it may require less binding resin than normal. Also, the copper ammonium acetate-oil complex may be added to green wood either in solid or flaked form.

Bio-oil produced by pyrolysis of non-conventional raw materials like palm fruit shells was characterized and positively tested as wood preservative agent (Sunarta et al., 2011). The pyrolytic liquid yielded at a ratio of 35% - 37% by weight of the waste material was effective against drywood termites (Cryptotermes spp.) and particularly against the blue stain fungi (Ceratocystis spp.).
Forest residues such as wood and barks from oaks and pines were subjected to thermal degradation to produce bio-oils, and subsequently fractionated to obtain lignin-rich fractions, consisting mainly of phenols and neutrals fractions. Whole bio-oils and their lignin-rich fractions were studied as potential environmentally benign wood preservatives with antifungal properties to replace metal-based chromated copper arsenate (CCA) and copper systems. At relatively high loading level (25%), the raw bio-oils showed excellent wood preservation properties. However, prevention of leaching is very critical to provide decay resistance (Mohan et al., 2008). Other organic residues may have potential use as raw material for producing oils and vinegars as wood preservatives, fungicides, herbicides, repellents and insecticides (Tiilikala et al., 2010).

Adding linseed oil increases boric acid retention; it also reduces leachability and improves efficacy against termites (Lyon et al., 2007a). The ammonium borate oleate (ABO), a complex product from the reaction between boric acid, ammonia and oleic acid, was positively tested as a wood preservative treatment against white and brown rot fungi (Lyon et al., 2009), and also resulted effective against termites (Lyon et al., 2007b). Efficiency of the ABO salt is based on the repellence provided by fatty acids, which deters boron leaching and penetration of water and fungi. This may be considered a dual treatment from the successful combination of coating and biocide products. In this case, the vacuum leaching procedure is inappropriate to place specimens in real exposure conditions because it forces penetration of water. This observation has reminded the lack of standardized procedure of testing for combined coating and biocide treatments.

A traditional method to preserve wood in Asian countries such as Indonesia is by smoking samples, which is an indirect way to apply wood condensates into the samples. Wood burning produce smoke that contains a variety of toxic polycyclic aromatic hydrocarbons (PAHs), as well as phenols, aldehydes, ketones, organic acids, alcohols, esters, hydrocarbons and several heterocyclic compounds (Stołyhwo and Sikorski 2005). When treating wood with smoke, moisture content is reduced and PAHs are condensed and diffused inside wood structure. PAHs have shown to provide some resistance to biological deterioration driven by termite attack (Hadi et al., 2010), and microorganisms Aeromonas hydrophila and Listeria monocytogenes (Sunen et al., 2003).

**COMBINED METALS AND BIOCIDES**

Combined use of certain metals acting as chelators with organic biocides might enhance their efficacy. Some metals are key components on fungal enzymes because they function as co-factors, and metal chelation may reduce the wood decay by fungi. Therefore, it is important to find the right combination of metal chelators and biocides that promotes the required synergistic action. Another approach is to increase the efficacy of organic biocides with antioxidant additives that synergically can scavenge the free radicals action of wood degrading microorganisms. In doing so the fungal activity may be successfully slowed down. Paradoxically, organic preservatives may be unstable with time. Thus, we need to understand the impact of different environmental conditions on the viability of the active ingredients, which may be susceptible to degradation by the same wood decay action or parallel mechanisms. These may include evaporation, water leaching, chemical or biological degradation of either the biocide or the formed biocide-wood complex, and photodegradation. Consequently, a protection additive has to be considered (Ruddick, 2008).

**TANNIN-METAL COMPLEXES**

One of the original classical patents was filed by Laks (1991) affirming that complexes of sulphated tannin extracts and copper (II) ions effectively protect wood against fungal attack. The complex can be impregnated into wood in a single step treatment using a water/organic solvent system, or formed in situ by treating the wood with an aqueous solution containing the extract and subsequently treating the wood with an aqueous solution of a copper (II) salt. This was based on sulphide derivatives of catechins from condensed tannins that have shown a
broad biocidal spectrum. Particularly, epicatechin-4-alkylsulfides and cupric complexes containing up to 20, and preferably 5 to 15 carbon atoms, were particularly effective against wood rotting fungi and gram-positive bacteria. Such sulphides were prepared by reacting condensed tannin, either in the form of purified tannin extracts or pulverized plant tissues, with an appropriate thiol reagent under mild acidic conditions (Laks, 1990).

Later, Lotz (1993) proposed the use of impregnating agents such as halogenated tannin extracts from plant species, which are relatively more resistant to fungi, weathering, rotting, and insect attack. The tannin extracts were converted to their halogenated products and absorbed by the treated wood samples. The halogenated tannin material may be used with other treatment agents such as fixatives or metal salts. In this case, Bromine was suggested as the preferred halogen material, with optimum treatment occurring at bromine concentrations above 2%, but preferably around 4% - 5%.

The mechanism of preservation by chemically modified tannin and tannin-ammonia-copper agents was examined by Yamaguchi and Yoshino (2005). Wood decay by Fomitopsis palustris was markedly suppressed by treating wood with the modified tannins agents, although the mycelial growth and the protein generated slightly increased. The preservative effects of the chemically modified tannins were attributed to inhibition of the enzymatic breakdown of wood components by xylanases, mannases and cellulases. No pH drop was observed in the culture medium, where the treated wood powder was set, implying negative production of oxalic acid, which is distinctively produced by F. palustris. The mechanism proposed was the chelation of copper, an essential trace element for wood decay by the brown rot fungi, by the tannin, and the neutralization or suppression of oxalic acid production by the ammonia-copper involved in the chemical preparation.

Synergic effect of natural product with an inorganic fungicide, and waste product upgrading were conceptualized by Lomelí-Ramírez et al. (2012) in the use of phenolics from coconut tree residuals for wood protection. Tannins extracted from the fibrous mesocarp of coconut, an agro-industrial waste, were tested satisfactorily along with copper salts addition against Trametes versicolor. The bioassays showed poor fungal inhibition for the wood samples impregnated only with the tannin extract. However, the tannin–copper complex mixture showed greater fungal inhibition due mainly to the retention values and the phenolic nature of solutions.

Currently, the tendency seems to develop processes that incorporate biocides into wood or wood products, but the biocide is presented as a nanoparticle. The biocide as a nanoparticle is applied into the wood or wood particles applying sufficient pressure to force it to penetrate into the wooden material (Laks and Heiden, 2004). Nanotechnology is promising for wood preservation; as well nano-metal treatment may be totally different from the traditional elemental metals treatment and perform in a different way. Nano-metals have characteristic size and charge that may improve their performance in wood protection applications. If their particle size is smaller than the diameter of pores in the bordered pits or in the wood cells, complete penetration and uniform distribution in wood can be reached.

FUNGICIDES USED FOR WOOD PROTECTION
Fungicides are organic or inorganic substances, natural or synthetic agents, acting against fungi. Their toxicant or retardant mechanism of action depends on their chemical structure and bioactive functional groups from which all important biocidal properties are derived. Some fungicides may present combined bactericidal, insecticidal or other biocidal effects, as boric acid does (Lloyd et al., 1990). In searching for natural fungicides, they should fulfil the mentioned properties as shown in table 1.

Fungicide efficacy is not a constant parameter because is influenced by more biological and environmental factors inside and outside of the fungal cells. Also it depends on its ability to impair fungal cells, suppress growth, and inhibit enzymatic or other actions from rotting-fungi on wooden substrates. The reference for field and lab tests is the critical minimal concentration (%) or the minimal critical retention in wood (kg/m³) (Reinprecht, 2008). Distinctive parameters to consider are shown in table 2.
### Table 1. Antifungal activity, mechanisms and uses of fungicides for wood preservation*

<table>
<thead>
<tr>
<th>Actions</th>
<th>Mechanisms</th>
<th>Fungicide applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Inhibition of respiration.</td>
<td>Inhibition of Acetyl coenzyme A (CoA).</td>
<td>Cupric ion Cu²⁺ from copper sulphate, copper oxide, copper naphthenate, copper-8-hydroxyquinolinate, Cu-HDO.</td>
</tr>
<tr>
<td></td>
<td>Fungal cells have affinity to different chemical groups (i.e., thiol groups), resulting in non-specific denaturation of proteins and enzymes.</td>
<td>Interruption of respiratory chain phosphorylation. Similar inhibitory effects from arsenic compounds, 2-phenylphenol, pentachlorophenol and other phenolic compounds, carboxamides, tributyltin compounds, or isothiazolones.</td>
</tr>
<tr>
<td>2. Inhibitors of polysaccharide biosynthesis</td>
<td>Inhibition of carbohydrate, protein, lipid and nucleic acid biosynthesis.</td>
<td>Polyoxins and antibiotics from streptomycete (Inhibition of chitin synthesis in fungi cell walls). Imidazoles, pyrimidines, triazoles (suppression of lipid synthesis).</td>
</tr>
<tr>
<td>3. Inhibitors of cell division</td>
<td>Inhibition of microtubules synthesis.</td>
<td>Benzimidazole derivatives (e.g. carbendazim, benomyl) interfere with microtubule subunit polymerization, preventing mitosis and depressing the DNA synthesis.</td>
</tr>
<tr>
<td>4. Disruptors of fungi cell membranes</td>
<td>Structure and function of sterols (i.e., Tiazoles (e.g. azaconazole, propiconazole, tebuconazole). Inhibition of sterol biosynthesis is connected with disruption of cell membranes.</td>
<td>Tar oils disrupt cell membranes dissolving lipids in membranes. Quaternary ammonium compounds (QAC) can rehydrate and damage the semi-permeable membranes of fungi (e.g. didecyl-dimethyl-ammonium chloride-DDAC), combined with leaking of cell constituents.</td>
</tr>
<tr>
<td>5. Enzymes inactivation</td>
<td>Simultaneous inhibition of metabolic activity, enzymatic functions and growth of fungi.</td>
<td>Hg²⁺-based fungicides, dicarboximides (reaction with thiol groups in proteins). Hg²⁺ and Cu²⁺ cations (Inhibition of glycolysis). Boric acid and boron compounds form stable complexes with vitamins, coenzymes or biological molecules with poly-OH groups (action as fungistatic rather than fungicide) (Lloyd et al. 1990).</td>
</tr>
<tr>
<td>6. Retardants of Fenton polysaccharides depolymerisation</td>
<td>Polysaccharides in wood cells chemically bond Fe⁺⁺ ions</td>
<td>Tropolon, β-tujaplicin (inhibit activity of brown-rot fungi) (Gérardin et al. 2002).</td>
</tr>
<tr>
<td>7. Retardants of fungal spread in wood</td>
<td>Adaptive nitrogen redistribution mechanisms, which are unique in rot-fungi</td>
<td>Non-toxic amino acid analogue “AlB” α-aminoisobutyric acid (Watkinson and Tlalka 2008).</td>
</tr>
</tbody>
</table>

*Prepared from Reinprecht (2010).
**Fungicide adsorption rate on the surface of fungal cells**

Rate of adsorption depends on physicochemical variables such as pH of wood.

**Fungicide accumulation rate into fungal cells**

Retention of fungicide by fungal body can be enhanced in presence of conditioners.

**Fungus species**

Individual fungi commonly show selective resistance to particular chemical fungicides.

**Fungal cells biomass**

Fungicide may be inactivated when interacting with fungus, thus it has to be applied at higher concentration than for preventive use.

**Fungicide retention/concentration and synergistic applications**

Minimal critical retention or critical minimal concentrations are not usually effective for a long time. Fungus can be adapted to the fungicide and other substances may catalyse or retard efficacy of the fungicide.

**Environmental factors: Temperature, Moisture Content, UV radiation, and others**

Abiotic factors influence activity of fungal cells. Extreme temperatures may inhibit or kill cells; warmer and wetter conditions may assist fluid diffusion of water soluble fungicides.

**Tabla 2. Parameters of fungicides efficacy in wood treatment**

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**BIOLOGICAL CONTROL OF WOOD DEGRADATION**

The main biological pests for wood preservation are fungi and insects. These biotic factors cause negative effects in wood quality mainly by decay and staining damages. Degradation may starts when wood is in contact with soil or water and cell wall polymers is attacked by bacteria. Complementary, handling practices and environmental conditions are influential factor to be observed. While chemical protection of wood products is effective in many cases, it imposes recognized ecological and health risks. Therefore, strategies for developing biological control agents are welcome as soon they are specific at targeting biological hazards and are readily biodegradable. Though, since they are living materials and have limited shelf-life, their design and formulation must be improved (Mai et al., 2004).

Attempts of biocontrol of wood deterioration with fungus such as *Trichoderma harzianum*, was evaluated by Canessa and Morell (1997) on ponderosa pine sapwood wafers at small-scale tests. Although this ascomycete fungicide significantly reduced the weight losses and the enzyme activities associated with white-rot fungi (*Trametes versicolor*) and brown-rot (*Gloeophyllum trabeum*), it could not completely inhibit their activity. Results suggested that these biocontrol organisms might inhibit slowly but not totally the decay process. Addition of sugars as carbon source has not enhanced the specific activity of the biocontrol fungus. Another example is the dry-rot fungus *Serpula lacrymans*, which is a typical brown-rot basidiomycete found particularly in woods under certain environmental conditions. Some *Trichoderma* isolates prevented *Serpula* colonisation in experimental wood-block tests. However, the biocontrol fungicides could not stop decay of already infected blocks, making the isolates only valid for prevention (Score et al., 1998). The antagonism mode of action appears to be the inhibitory volatile organic compounds produced by the *Trichoderma* isolates (Humphries et al., 2002). The production of volatiles by *Trichoderma* is determined by cultural age and medium composition, and mainly by the amino acids available (Bruce et al., 2000). It
is known that aldehydes and ketones of seven to ten carbons such as heptanal, octanal, nonanal and decanal and related ketones inhibit growth of a wide range of brown and white-rot fungi. Extended protection by *Trichoderma* or other fungal antagonists is likely not achievable, but at least a certain prolongation of the life-time of wood products is feasible. Experiments to protect wood against decay fungi by antagonist action of other microorganisms are still under exploration and evaluation.

**INSECT BIOCONTROL**

Some novel methods for coating, penetrating, treating, and curing wood, wood composites or cellulosic materials are inspired in the addition of natural biocides such as azadirachtin from seeds of the Neem tree (*Azadirachta indica*), where is present at 0.2% - 0.8% (Subbaraman and Brucker, 2001). This component disrupts the feeding behavior and growth cycle of termites, wood-borers and other biologically important insects. The water resistant formulation contains the Neem seed oil plus binding and bittering agents, which enhance the long active effectiveness of the extract. The composition is non-reactive, non-toxic to vertebrates, and non-polluting of surrounding soils. Also, the preparation may be resistant to oxidation, and photo degradation, when applied in non-aerobic conditions, such as subterranean use. Azadirachtin as well other specific insecticidal and fungicidal compounds are found also in the leaves and bark of the neem tree. Therefore the plant becomes an available source of biocides and a compatible biological control option against other pest insects (Nathan *et al.*, 2005).

In other paper, Neem extracts alone or mixed with copper sulphate and boric acid confirmed their antifungal activity protecting mango (*Mangifera indica*) and rain tree (*Albizia saman*) woods (Islam *et al.*, 2009). The Neem extract treatment has been extended with relative success against beetles and termites because these woods are widely used in Bangladesh and are very susceptible to them, as well to decay and wood-staining fungi. The growth of white rot fungus (*Schizophyllum commune*) was fully inhibited on field samples containing 1.8% of the extract or 5% from the mixture. The average weight losses were significantly lower compared to the controls, providing an increase of 6–7 times on the life span. Therefore, these are promising treatments for tropical woods preservation. Similar studies have concluded on the efficacy of cashew nut shell liquid against termites in the termite mound compared to the conventional creosote treatment (Jain *et al.*, 1989).

Another tree with potential phytochemicals is Camphor (*Cinnamomum camphor*), which is rich in camphor, eucalyptol, terpineol, linalool, and 4-terineol, active compounds already used in medicines and insecticides (Liu *et al.*, 2006). Particularly, camphor leaves extract, which is thermally unstable and volatile but has strong insecticidal and antifungal activity, is mixed with fixing agents to facilitate the protection action in bamboo. Some polymers have been used as modifiers to improve the durability of treated wood. As an example, Melamine-modified Urea Formaldehyde resin prepolymer (MUF) have improved the mechanical strength and decay and insect resistance of treated wood and bamboo samples compared to controls (Xu *et al.*, 2013). These resins are efficient fixative materials for plant-based preservatives, keeping their activity and improving their thermal stability.

**COMBINED PROCESSES**

The co-addition of the synthetic antioxidant BHT (butylated hydroxytoluene) increased the efficacy of wood samples treated with the commercial fungicides Propiconazole/tebuconazole or DC01 in an accelerated soil-contact test (Schultz and Nicholas, 2011). Parallelly, the natural antioxidant and metal chelator propyl gallate improved the response of above ground samples treated with propiconazole and wax. These experiments highlight the antioxidant and metal complexing properties of organic phenolic extracts that protect wood from decay when combined with biocides.

The addition of heartwood extractives such as walnut tree has being explored with relative success in combined systems based of acid copper chromate, and boric acid tested on beech sapwood for white rot fungus resistance (Feraydoni and Hosseinihashemi, 2012). Substances such
as juglone, 2,7-dimethyl phenanthrene, and gallic acid from walnut heartwood flour have been reported with antifungal activity (Hosseinibashemi and Latibari, 2011).

In cooper based preservatives, the use of rosin has being proved as good fixing agent. Rosin is a paper sizing agent from softwoods that has a suitable hydrophobic character and affinity for the wood structure. This feature is appropriate to maintain a low moisture absorbing tendency and help to keep cooper from being leached out (Hien et al., 2012).

Boron compounds are recognized as good wood preservatives, acting as both fungicide and insecticide, relatively inexpensive and environmentally acceptable (Caldeira, 2010). However, in the field, borates are used only for indoor and non-exposed applications or in combination with other biocides, because they are easily leachable from treated wood (Thevenon et al., 2009). The fact is that boron is not fixed chemically to wood, and it will be leached out if wood in service if subjected to any wet environment, even at moisture contents below 20% (Peylo and Willeitner, 1995). This boron leaching, which is a major drawback, has being markedly reduced in wood preservatives based on the cross-linking and hardening of condensed tannins with hexamine, where boric acid was added and formed a composite. Boron can be covalently fixed to the tannin-hexamine network (Tondi et al., 2012a). As a desired output, the wood treated with this system has shown a significantly enhancement of wood durability before and even after leaching once tested towards basidiomycetes (Thevenon et al., 2010). The mechanical and fire-proofing attributes of pine and beech specimens preserved with these formulations were improved. Treated samples under compression, bending, hardness, and gluing tests showed average improvements of 20%. The treatment with tannins has enhanced the fire resistance of samples, which was also upgraded with the addition of boron and phosphorous (Tondi et al., 2012b). Eventually more work on this concept such as impregnation, agent diffusion, and wood anatomy considerations (Tondi et al., 2013), may lead to effective, more environmental and friendly wood protection systems.

**ENVIRONMENTAL CONCERNS AND BIOTECHNOLOGY**

Environmental concerns have stimulated the search for friendly substitutes to replace toxic chromium and arsenic in chromated copper arsenate (CCA) systems by soy products in wood preservative formulations (Yang et al., 2006). Soy is intended as chelating and fixative agent in preservative solutions containing anhydrous cooper sulphate and hydrated borax. Despite the molecular sizes of the copper–protein and copper–boron–protein complexes, pine samples were treatable, leached and exposed successfully to brown rot fungi. Although wood samples needed higher retentions, soy-based formulations should be still evaluated by long-term ground-contact testing to consider them as an optional wood preservative from fungal attack and replace of CCA.

Another original approach for ecological preservation of wood materials is the copolymerization of phenolic extracts from pine barks with acrylic monomers into the cell wall structure (Dumitrescu et al., 2008). Besides the biocide effect there is a plus regarding the emulsifying capacity from the bark extract, which improves the emulsion stability.

Traditionally, Biotechnology has found little attention in the forest products industries, and particularly in the wood preservation field. Now, the situation is changing due to legal restrictions on conventional processes detonated by growing environmental concerns and a favourable scientific background. Current biotechnological approaches for wood protection are targeting to the treatment of wood with natural and ecological friendly preservatives and replacing conventional chemicals with biological control agents.

Complementary, Biotechnology is playing an important role in the remediation of wastes from chemically treated wood. Developing of low environmental impact technologies to remove any biological damage is still one of the major goals of wood protection industry. An example in this sense may be the experimentation for potential recycling of old creosote-treated woods through a pyrolysis process to produce tar oils for treating new wood ele-
ments. Wood tar obtained this way may have potential as a sustainable preservative for wood protection or as a component of preservatives (Mazela, 2007).

**CONCLUSION**

At present time, several types of inorganic and organic fungicides are commonly used for protection of wood products against termites, moulds, staining and rotting fungi. However, in the near future the wood preservation industry is required for sustainable processes based on environmentally more friendly additives. Among the most expected biocides are natural substances such as tannins, chitosan, and plant oils, maybe in combination with synthetically prepared organic compounds such as heterocycles and carbamates. Research in this field is becoming complex as chemical modification of the wood structure and the treatment with nanomaterials are promising tools that will change the actual view and performance of wood preservation industry and their methods.

Moreover, wood preservation processes focus on standard chemical treatments are part of the innovation efforts from chemical companies. They are looking for differentiating wood products with no current value-added, giving them colouring, finishing and chemical treatments.

Besides the ecological impact of residues and the required approach to environmental sustainability, in the next years, biotechnology industries will put more attention on organic/inorganic wastes as a valuable source of energy or new biomaterials. Particularly, biowaste evaluation will be carried out on wood processed wastes, for further testing and validation at larger scale. These biocconversion processes have to be integrated, combining biomass treatments, energy production and/or recovery of useful biochemicals.

Finally, a modern vision will consider nanotechnology to improve raw materials and enhancing resistance and durability to decay. Consequently, a priority will be developing products with value-added and functionality to existing products and designing novel nanotechnologies for new generations of more cost effective wooden products. The nanotechnological applications have great potential to improve treatability of commercially important wood species, designing engineered composites and delivery systems for specific targeted applications such as developing of slow-release of combined metal and biocides models. At the end is clear that the goal is offering to the market only safe, stable and effective products, i.e., with economic and environmental sustainability.

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