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Copper and boron fixation in wood by pyrolytic resins

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ABSTRACT

A phenol–formaldehyde (PF)-resin designed to penetrate wood and immobilize copper and boron in wood cells for protection against decay was investigated. The phenol portion of the PF-resin was partially substituted with pyrolysis oil derived from softwood bark. The objective was to reduce the environmental impact associated with the production of petroleum-borne phenol, as well as to improve the product economics. Leaching tests were conducted with three different formulas of resins containing 50%, 75% or 85% by weight of pyrolytic oil on a total phenol basis. The leachates were analyzed for the presence of copper by atomic absorption spectroscopy while inductively coupled plasma spectroscopy was used for boron detection. Copper leaching was reduced up to 18 times when comparing the treatments with and without the resin. Preservative leaching varied between wood species as well as between the resins containing different concentrations of pyrolytic oil. The organic leachates were measured using gas chromatography and mass spectroscopy. Trace amounts of organics, mostly acetic acid, were found in the leachates.

1. Introduction

Chromated copper arsenate (CCA) was withdrawn by the industry as a wood preservative for residential use in North America at the end of 2003 due to public concerns about the toxicity of arsenic contained in the preserving agent. For the time being, the CCA alternatives are copper-based chemicals such as amine copper quat (ACQ) or copper azole (CA), but considerable research is under way to find alternatives. Leaching of copper from treated wood to the environment will become an increasingly important issue for the wood preservation industry. So far, none of the new wood treatments using copper offers the prospect for long-term fixation of copper.

Copper is a wellknown fungicide and is widely used in the formulation of preserving agents. Products such as alkaline copper quat (ACQ), amine CA and copper bis-(*N*-cyclohexyldiazeniumdioxy) (Cu-HDO or copper xyligen) are currently the main CCA alternatives (Evans, 2003; Freeman et al., 2003). However, certain applications of wood treated with one of those alternatives in wet conditions (docks and pilings, for example) might result in more substantial leaching of copper than would occur from CCA-treated wood (Waldron et al., 2003). Losses of copper and other compounds from treated wood preservatives poses a concern due to environmental pollution, health hazards and potential for reduced protection against biodeterioration. Copper toxicity to aquatic organisms has been well documented and is a concern for the use of copper-containing wood preservatives in aquatic environment (Weis et al., 1991; Hingston et al., 2001; Weis and Weis, 2004).

Boron-based products have also emerged as alternatives to fill the gap created by the CCA removal. Boron is effective against both fungi and termites and possesses low mammalian toxicity; however, boron is leachable, which restricts its use to applications where the wood will stay dry (for example, indoors). Much research is oriented toward the fixation of boron in wood or reducing its release (Thevenon et al., 1998; Yalinkilic et al., 1998; Gezer et al., 1999; Toussaint-Dauvergne et al., 2000; Evans, 2003). Boron has been observed to leach less when used with an excess of copper (Richardson, 1993), and the combination of copper salts and boron salts in treated wood applications has been patented (West, 2001).

Resins may be an efficient way for immobilizing preservatives in the wood (Lewis, 1995). Ryu et al. (1991) impregnated phenol–formaldehyde (PF)-resins in wood and observed increased resistance to biodegradation. They also observed a relation between resin molecular weight and performance (Ryu et al., 1993). Low molecular weight PF-resins penetrate cell walls following wood impregnation, contributing to both dimensional stabilization and resistance against decay (Furuno et al., 2004). Similar

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observations have been made with a phenol–resorcinol–formaldehyde resin (Gindl et al., 2004). The mechanisms involved in this increased resistance are not yet fully understood, but might involve increased hardness or altered moisture relationships.

Pyrolytic oils have been tested in the formulation of PF adhesives for panel manufacturing as a means for reducing the consumption of petroleum-borne phenols (Chan et al., 2002). It is known that copper, when added to resins, will accelerate their curing time (Pizzi, 1979). Gagnon et al. (2003) showed that, for OSB panel production, addition of around 35% of pyrolytic oil in a polymethylene diphenyl diisocyanate (pMDI) resin was the best ratio for curing. Chan et al. (2002) fabricated two kinds of OSB panels with PF-resins containing pyrolytic oil as a phenol replacement at ratios of 25% and 35%. Higher concentrations (50%) decreased the performance of the resin in terms of cure kinetics and extent of condensation (Amen-Chen et al., 2002).

Pyrolysis is the thermal decomposition of a solid fuel (such as biomass) in the absence of oxygen. A number of pyrolysis processes exist, some operated under vacuum such as the Pyrovac™ process (Roy et al., 2001). Most processes, however, involve a carrier gas, usually nitrogen. The end-products are charcoal, incondensable gas and pyrolytic oil. The composition and quality of each product depends on the chemical nature of the biomass, the size of the particles fed in the reactor, the temperature, the residence time, the moisture content of the feedstock and a number of other parameters (Pakdel et al., 1997; Diebold, 1997).

Oils obtained from biomass pyrolysis have the potential to become an innovative wood preservative. Suzuki et al. (1997) attributed the antifungal properties of pyrolytic tar mostly to four phenolic compounds. Two of the compounds identified by the authors were also found in pyroligneous liquors tested by Mourant et al. (2000) against decay fungi. Freel and Graham (2000) explored the use of pyrolytic oil as a preserving agent and a petroleum substitute in creosote. Although pyrolytic oils can prevent fungal growth under laboratory conditions, the organic compounds in the oils are leachable when used as a wood preservative without additives or modifications (Meier et al., 2001; Mourant, 2001).

This project aims to develop a bio-oil-based resin to fix or reduce the leaching of copper and boron used as wood preservatives. As a positive side effect, copper acts as a curing accelerator of the resin itself. This paper presents results of a study on the comparative leachability of organics, copper and boron from sapwood blocks treated with three resin formulas after being treated with either a copper chloride or a copper chloride–borax solution following the AWPA E10-06 (2006) standards for testing new wood preservatives. Resin-coated samples were compared to blocks treated with either CCA type C, ACQ, the copper chloride solution, the copper chloride–borax solution or the resin alone.

2. Methods

2.1. Pyrolysis of softwood bark

A bark mixture composed of balsam fir (*Abies balsamea* – 70%) and white spruce (*Picea glauca* – 30%) was air dried to a moisture content of 16.5% before being shredded to a mesh size of less than 25 mm. The pyrolysis run #H68 was performed at 450 °C and at a total pressure of 20 kPa in a process development unit at a throughput capacity of 34 kg/h. The detailed pyrolysis process and equipment has been described elsewhere (Roy et al., 1997, 1999; Yang et al., 2001). A chemical characterization of the pyrolysis oils used in the resin formulations is given in Table 1.

Table 1

Typical chemical composition of pyrolysis oils obtained from pyrolysis of softwood bark residues (reproduced from Chan et al. (2002))

Family of compounds	Concentration in total oil (wt%, anhydrous basis)
Hydrocarbons	3
Sugars	9
Low-molecular weight-acids	1.5
High-molecular weight-acids	10
Alcohols	2.5
Esters and ketones	4
Phenols	10
Steroids and triterpenoids	4
Lignin/tannin-based compounds	48
Labile compounds	8
Total	100

2.2. Resin synthesis procedure

Aqueous formaldehyde at 37% by wt concentration and phenol were added together at a ratio of 2.5:1 in a kettle equipped with a mechanical stirrer. After homogenization, a 50% by wt NaOH solution was added drop-wise to obtain a phenol:NaOH ratio of 1:0.15. The whole mixture was heated to 65 °C in about 15–20 min and kept at that temperature for 100 min. The mixture was cooled to 30–40 °C and a determined amount of formaldehyde scavenger (NH_4OH at 28% by wt) was added. The final viscosity of the PF-resin was 20 ± 1 cP at 25 °C. The various treating resins were obtained by mixing the PF-resin with pyrolytic oil at different ratios of substituted phenol. Phenol substitutions tested were 50%, 75% and 85% on a weight basis, hereafter named R350, R375 and R385 according to the percentage of pyrolytic oil present. The resins were stored at 4 °C until needed.

2.3. Treatment of wood blocks

Impregnation of the preserving solutions into the wood samples was conducted in two sequential treatments, i.e., copper chloride or copper chloride/sodium borate mixture was impregnated first, the resin being impregnated afterwards. Earlier results obtained in this lab showed that this method of treatment resulted in the best penetration into the samples.

White pine (*Pinus strobus*) and American beech (*Fagus grandifolia*) sapwood blocks (14 × 14 × 14 mm) were oven dried at 105 °C and weighed. One hundred and ninety two blocks of each species were placed in a beaker with a 5% copper chloride ($CuCl_2 \cdot 2H_2O$) solution and vacuum impregnated for 30 min at 14.7 kPa. The blocks were then left at atmospheric pressure for an hour before being oven dried at 105 °C and weighed. Additionally, 192 blocks of each species were treated with a mixture of copper chloride and disodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$) solution (5%:2%) using the same conditions described for the copper chloride solution alone. The treated blocks were then placed in beakers (six per jar) containing one of the three resins and subjected to a thirty min vacuum (61.3 kPa) followed by a one hour pressure period (550 kPa). The blocks were allowed to bleed the excess of resins for an hour before being brushed free of surface deposits and cured overnight at 105 °C. Table 2 summarizes the various formulations tested. The blocks were weighed and leached in glass jars, six pieces per jar, four jars per treatment (total of 24 blocks/treatment), based on procedures described in the AWPA standard E10-06 (AWPA, 2006). Only half the treated blocks were leached, while the remaining were kept for decay resistance studies. Fifty milliliter aliquots of leaching water were retained per leach cycle to be analyzed sequentially for copper, boron and organic