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A wood treatment based on siloxanes and boric acid against fungal decay and coleopter *Hylotrupes bajulus*

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ABSTRACT

A wood preservative based on tetraethyl orthosilicate (TEOS), 3-aminopropyltriethoxysilane (APTES), and boric acid (BA) in volume ratio TEOS/APTES 1:1 and in molar ratio APTES/BA 50:1 was applied to wood by the sol–gel process. Standard EN 113 and mini wood block tests were carried out to determine the effectiveness against fungal decay. The same formulation applied by immersion was tested against larvae of the wood-borer insect *Hylotrupes bajulus*. This formulation showed good efficacy against *Coniophora puteana*, *Poria placenta*, and *Trametes versicolor*, even after a leaching procedure. It was also effective against the coleopter *H. Bajulus*. Different molar ratios of APTES/BA—2.5:1, 5:1, and 10:1—were tested with a leaching procedure in accordance with EN 84 to determine the best fixation of boric acid into the wood. The ratio APTES/BA 5:1 was found to be the most effective for fixing boron into wood.

1. Introduction

Boric acid is effective against fungi and xylophagous insects and it is also considered non-toxic to humans and the environment if used under the limit indicated in Biocidal Products Directive 98/8/EC (European Commission, 1998). The recent classification of boric acid and borates as toxic to human reproduction, category 1B according to the EC Regulation 790/2009 (European Commission, 2009) means that they fall within the scope of the measures of risk reduction provided by the REACH regulation (European Parliament, 2006). The justification for the use of boric acid and borates is linked to the fact that the repro-toxic effect occurs at a threshold concentration of 5.5%. Below this value these substances are considered safe.

The main advantages of boron (B) are its high level of efficacy and broad spectrum of action (Nunes, 1997; Humar et al., 2007). The minimum efficacy concentration values for different fungal and insect species are reported by Kartal et al. (2007) and Lesar and Humar (2009).

Nevertheless, this substance alone cannot be applied to wood exposed to atmospheric agents because it is easily washed away into the ground. This is why various strategies to achieve boron fixation have been developed, although very few have been successful so far (Obanda et al., 2008; Caldeira, 2010).

Recently, wood has been successfully modified with mixtures of siloxanes provided with amino groups with a copper linking function through a sol–gel process (Palanti et al., 2011). Tetraethyl orthosilicate (TEOS) and 3-aminopropyltriethoxysilane (APTES) were used as precursors; their hydrolysis and co-condensation (the sol–gel process) was allowed to take place in situ. This process generates hybrid inorganic-organic silica xerogel particles penetrating the wood cell walls. The deep interpenetration of the functionalized xerogel in the wood texture was evidenced by SEM–EDS investigations (Vignali et al., 2011). The same kind of investigations, together with X-ray mapping, also demonstrated that copper anchored to NH_2-R-funtionalized silica xerogel is drawn into wood (Palanti et al., 2010; Vignali et al., 2011). X-ray maps revealed that silicon is present mainly on the cell walls. A high degree of condensation for wood specimens treated with the TEOS/APTES combinations and for the treating xerogel was detected through solid-state NMR investigations; this suggests that polymerization of the siloxanic matrix into wood is quite complete and

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will not change significantly upon ageing (Vignali et al., 2011). Unfortunately, this technique was not to able to detect the existence of a real chemical bond between wood and the silica matrix.

The combination TEOS/APTES 1:1 proved to be the best one to confer durability against *Coniophora puteana* (Palanti et al., 2010). These previous findings suggested a combination of the fixing properties of alkoxysilanes with the biocidal properties of boric acid, with a test of the new formulation to see how it performed against fungi and insects. For this purpose, a preservative based on tetraethyl orthosilicate (TEOS), 3-aminopropyltriethoxysilane (APTES), and boric acid (BA) was tested for leachability and biodegradation susceptibility.

Boric acid is supposed to interact with the silica xerogel in two ways: by condensation with silanol groups, giving rise to Si–O–B linkages (formation of borosilicates); and by formation of ionic interactions with the amino groups. Fourier transform-infrared spectroscopy with ATR on treated samples attested to the presence of Si–O linkages, showing an enlargement of the band around 1000 cm^{-1}, but no differences attested were seen in the interaction of boron with silica matrix (personal communication).

In this research different ratios of APTES/BA were tested with a leaching procedure to determine the formulation that gives the best fixation of boric acid into the wood. The combination of TEOS/APTES in a volume ratio of 1:1 and APTES:BA in a molar ratio of 50:1 was tested against biological decay in relation to the service life conditions of treated wood. For use class 3 (EN 335-1, 2006), the formulation applied by impregnation followed by leaching was evaluated against brown-rot and white-rot fungi through a mini-block and a standard test; concerning use classes 1 and 2, the formulation applied by immersion was tested against larvae of the wood-borer insect *Hylotrupes bajulus*.

2. Materials and methods

2.1. Wood samples

Pinus sylvestris L. sapwood was chosen, as this is the wood species required by the European Standards to test the effectiveness of a treatment against wood-destroying organisms (EN 113: 1996; EN 46-1, 2010). Two series of differing dimensions — $5 \times 10 \times 30$ mm^3 and $15 \times 25 \times 50$ mm^3 — were cut from boards. Wood samples subjected to the impregnation process had previously been oven-dried.

2.2. Treatments

Formulations made of TEOS/APTES in a volume ratio of 1/1 and boric acid in the molar ratios APTES/BA 2.5/1, 5/1, 10/1, and 50/1 were prepared. Ingredients were diluted in an equivalent volume of ethanol. Table 1 shows all the ingredients present in the four different formulations. The formulations were utilized for the leaching procedure in accordance with EN 84 (1997) and to determine the boron content on treated samples.

Table 1
The composition and quantities of the ingredients present in the formulations.

Formulations	APTES/BA	Ingredient	Molar concentration mol/l	Concentration w/w %
1-2-3-4	–	TEOS	1.3	28.7
1-2-3-4	–	APTES	1.1	27.1
1-2-3-4	–	Ethanol	8.6	42.8
1	2.5:1	BA	0.4	2.8
2	5:1	BA	0.2	1.4
3	10:1	BA	0.1	0.7
4	50:1	BA	0.02	0.14

For each formulation, the samples were impregnated in an autoclave applying 0.7 kPa for 15 min.

The wood samples were left soaking in the solution for 2 h; then they were extracted, wiped gently, weighed, and placed in the conditioning room. After conditioning the samples were oven-dried for 18 h at 103 °C and weighed again.

The vacuum-atmospheric pressure impregnation process was characterized through the determination of weight percent gain (WPG_1), calculated from the dry mass before and after treatment (Donath et al., 2004) according to the following equation (Eq. (1)):

$$\mathrm{WPG} = \frac{M_t - M_o}{M_o} \times 100 \quad (1)$$

where M_t and M_o are the oven-dry weights of sol–gel treated and untreated wood samples, respectively.

Formulation 4 was applied by dipping the wood specimens that were chosen for the insect test. Ten wood blocks, measuring $15 \times 25 \times 50$ mm^3 and conditioned to constant mass at 20 °C and 65% RH, were first sealed in transverse faces (15×25 mm^2), then soaked in the solution for 30 min. During immersion, they were ballasted to avoid floating. The difference between weight before and after immersion gave the uptake of the treatment; this value, expressed per area unit and measured as grams per square metre, corresponded to the retention, which was used to characterize the immersion process.

2.3. Leaching

Wood specimens impregnated with formulations 1, 2, 3, and 4 were subjected to the leaching procedure according to EN 84 (1997). Wood specimens were placed in a glass beaker filled with deionised water conforming to EN ISO 3696 (1996). Wood specimens were prevented from floating by the use of weights. The beaker was put in a desiccator under a 0.04 bar vacuum for 20 min. After returning to ambient pressure, wood specimens remained submerged for another 2 h. Subsequently, the leaching water was decanted and replaced nine times over a period of 14 days using a wood/water volume ratio of 1/5. After leaching and conditioning, samples were oven-dried again as previously described, and weighed. Weight percent gain after leaching (WPG_2) was calculated according to Eq. (1), where M_t is referred to dry mass after leaching.

The percentage of formulation that leached out during water immersion was calculated as a ratio between the differences in anhydrous masses prior to (M_t) and after (M_l) leaching (Eq. (2)):

$$\mathrm{LF} = \frac{M_t - M_l}{M_t - M_o} \times 100 \quad (2)$$

2.4. Measurement of boron

One or two samples (of standard dimensions) treated with each of the four formulations tested, for not leached and leached cases, were ground and then mineralized with 70% HNO_3 and 40% HF acid in a microwave oven for 45 min at 180 °C.

Quantification of boron was performed on both sets by inductively coupled plasma optical emission spectrometry (ICP-OES); an yttrium internal standard was used to correct any possible calibration error. Measurement was expressed in mg of boron per kg of dry matter.

2.5. Efficacy test against fungi

Both leached and untreated control specimens were γ-sterilised before fungal exposure. The European Standard EN 113 (1996)