Use of boron compounds for treatment of wooden historical objects

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Abstract

Boron compounds are still one of the most important active ingredients used for wood preservation. They are applied as fungicides as well as insecticides. However, most of efficacy data reported for boron efficacy are rather old, and thus in contradiction with new reports. Therefore, minimal inhibitory concentrations for boron were re-evaluated. Tests were on three brown (*Gloeophyllum trabeum, Serpula lacrymans* and *Antrodia vaillantii*) and three white rot (*Trametes versicolor, Pleurotus ostreatus* and *Hypoxylon fragiforme*) fungi. To inhibit growth of wood decay fungi, lower minimal effective retentions were determined than reported in previous publications. Furthermore, minimal remedial boron fungicidal concentration is comparable to the preventive minimal inhibitory concentration.

Key words: boron, boric acid, fungicidal properties, minimal inhibitory concentrations

INTRODUCTION

Boron compounds find extensive use in a wide range of industrial applications, nearly all involving boron-oxygen compounds. One of the important uses of boron is use in the field of wood preservation [1]. Moderate concentrations of borates can inhibit the growth of wood-destroying fungi and repel attacks by wood-boring insects, such as termites, carpenter ants, and beetle larvae [2]. The low mammalian toxicity of borates combined with their broad activity against organisms detrimental to wood makes them attractive in this application [3]. Boron compounds are besides being effective fungicides and insecticides, widely used in fire retardant applications as well. One of the important advantages of boron preservatives is fact that they produce few visual or structural changes in wood [4].

Boron compounds are one of the longest-used active ingredients that are still in use for wood preservation. After implementation of Biocidal product directive in 2006 [5], several classical active ingredients have been removed from the market, and boron-based formulations have turned out as one of the strongest alternative in the field of wood preservation [6]. Thus their importance increased significantly. Boron compounds have low mammalian toxicity but, they are very effective against most of wood pests. Their use is limited due to its diffusibility and susceptibility to leaching [7]. This is the main reason why boron cannot be applied for outdoor applications without additives or surface coatings that reduce boron leaching [8].

Wood preservatives, based on boron compounds are very effective for remedial treatment of wood as well. They can be applied by various techniques like spraying, dipping, brushing, injection… The most important advantage of boron based biocides is that they are soluble as in water as well as in methanol and ethanol. Boron compounds are well absorbed by the wood surface and then penetrate by diffusion dipper into the wooden objects. Therefore they are particurlarly suitable for treatment of covered historical objects, that can not be treated by other procedures. In a number of studies, boron compounds have moved well through moist wood, but move very little when the moisture content falls below 30% [9]. Proponents of these systems have pointed out that substantial fungal decay does not occur when the moisture content falls below 30%, therefore, it should not matter if the diffusible compound does not move in dry wood since no decay can occur under these conditions [2].

Despite of the fact that boron compound are utilised for wood preservation for more than a century, there are not plenty information on their efficacy. Most of the efficacy data of boron compounds against wood decay fungi are rather variable [4,10,11,12] and are sometimes not in-line with novel results [13]. Thus, boron minimal inhibitory concentrations against wood inhabiting fungi were re-considered.

1. MATERIALS AND METHODS

Minimal inhibitory concentration of boric acid (BA) against fungi was determined in the nutrient medium and impregnated wooden blocks. For testing three brown rot (*Antrodia vaillantii, Gloeophyllum trabeum* and *Serpula lacrymans*) and three white rot (*Pleurotus ostreatus, Trametes versicolor* and *Hypoxylon fragiforme*). In the first part of research, diluted BA solutions were added to 20 mL of sterilized cooling potato dextrose agar to achieve different final concentrations as resolved from table 1. Solidified growth media were inoculated with 0.7 cm diameter pieces of mycelium. Fungicidal properties of BA ware calculated from ratio between radial fungal growth at BA-supplement and control Petri dishes after 10 days of incubation. Experiment was performed in five parallel Petri dishes per concentration/fungi.

In the second part of experiment fungicidal properties of boron impregnated wood were determined according to the modified standard EN 113 [14] procedure. Specimens in our test were slightly smaller than prescribed by standard. In order to achieve targeted retentions of boric acid, specimens (1.0 × 1.5 × 4.0 cm) were vacuum/pressure impregnated with different aqueous solution of BA (table 2). For impregnation standard full cell process was utilized. Beech wood (*Fagus sylvatica*) specimens were exposed to white rot fungi, and Norway spruce (*Picea abies*) ones were exposed to brown rot species. After 12 weeks of exposure mass loss of the decayed specimens were gravimetrically determined and expressed in percentages. Mass losses lower than 3% are considered insignificant according to the EN 113 protocol. Experiment was performed on five parallel specimens per targeted retention/fungi.

Furthermore, remedial properties of boric acid against wood decay fungi ware determined. In order to elucidate remedial efficacy of boric acid against wood decay fungi, initially wooden specimens (1.0 × 1.5 × 4.0 cm) were exposed to above mentioned fungi for six weeks. Similarly as explained above, beech wood blocks were exposed to white rot and Norway spruce specimens were exposed to brown rot fungal species. This period of exposure enable fungi to colonize and partially decay wood specimens. At this stage of decay, fungi are usually in the most vital state. After respective period of exposure, wood specimens were isolated and clean of fungal mycelium. Infested wood specimens were dipped to sterile boric acid solution of various concentrations and afterwards transferred to solid nutrient medium. In the next days fungal growth was monitored and visually estimated. Parallel specimens were not exposed to the fungi but they were used for gravimetric determination of retention of preservative solution.

2. RESULTS AND DISCUSION

As expected, boron exhibited good fungicidal efficacy against tested wood decay fungi. Similar as observed at copper compounds, lower concentrations (6.25 ppm – 12.5 ppm) of B in certain cases did not retard fungal growth, but in contrary promote it. This is expectable, as boron is well known essential element. In general fungicidal efficacy of boron biocides is much higher than of copper ones. To inhibit growth of the fungi growing on nutrient medium, at six of eight fungal species tested, 200 ppm of boron was necessary. For example, to inhibit growth of copper sensitive species 640 ppm and to inhibit growth of copper tolerant up to 1500 ppm of copper is required [13]. The most resistant white rot fungi *H. fragiforme* were inhibited at 400 ppm of B, while *P. ostreatus* was still growing at that high concentration. Experiments performed on nutrient medium showed, that white rot fungal species were slightly more resistant against boron than brown rot or blue stain fungi (Table 1).

Table 1: Influence of boron concentration in nutrient medium on retardation of fungal mycelia growth. Negative values indicate that growth of fungal mycelia in presence of boron was faster than on control nutrient media. Standard deviations are given in the parenthesis.

Fungal species	Boron concentration (ppm)							
	0	6.25	12.5	25	50	100	200	400
	Retardation of fungal growth (%)							
Antrodia vaillantii	0 (0)	6 (2)	4 (1)	6 (2)	10 (0)	82 (9)	100 (0)	100 (0)
Gloeophyllum trabeum	0 (0)	-8 (4)	-1 (1)	0 (2)	32 (9)	73 (7)	100 (0)	100 (0)
Serpula lacrymans	0 (0)	-3 (1)	0 (0)	-2 (1)	4 (1)	91 (6)	100 (0)	100 (0)
Pleurotus ostreatus	0(0)	-11(1)	-10(1)	-7(0)	-1(1)	-13(1)	8(1)	38(2)
Trametes versicolor	0 (0)	-14 (2)	-14 (2)	3 (1)	22 (4)	38 (4)	100 (0)	100 (0)
Hypoxylon fragiforme	0 (0)	0 (1)	0 (0)	0 (2)	0 (3)	34 (3)	96 (3)	100 (0)

A similar relationship is evident from the experiments performed on wooden blocks. The most boron sensitive species was *G. trabeum*. This fungus was inhibited at retention of 0.2 kg of BA/m^3. Furthermore, retention of 0.4 kg/m^3 was enough to inhibit growth of *A. vaillantii*, *S. lacrymans* and *T. versicolor*. However, white rot fungi *P. ostreatus* and *H. fragiforme* were found the most boron resistant fungal species in this part of experiments as well (Table 2). Retention of 0.8 kg/m^3 of BA were required to preserve wood against above mentioned fungi. From application point of view, it is very important that BA is more effective against brown rot species, that are more frequent in use class II and III applications, than white rots, as BA is predominately used for protection of wood in use class II and III as well. However, our results showed higher efficacy of boric acid against wood decay fungi in comparison to the data reported 50 years ago. Several authors reported that retentions between 0.52 and 2.88 kg of BA/m^3 are required to prevent wood against *G. trabeum* in laboratory conditions. Similarly, cited references reported, that up to 1.92 kg of BA/m^3 is necessary to stop decay processes of *T. versicolor* [4,7,10,11,12].

Table 2: Mass loss of the specimens impregnated with aqueous solutions of boric acid (BA) of various concentrations after 12 weeks of exposure to wood decay fungi. Standard deviations are given in the parenthesis.

B conc. (ppm)	Targeted retention of BA (kg/m^3)	*G. trabeum*	*A. vaillantii*	*S. lacrymans*	*T. versicolor*	*H. fragiforme*	*P. ostreatus*
		Mass loss (%)					
0	0	44.0 (5.9)	30.3 (6.7)	40.5 (7.0)	27.8 (4.5)	46.3 (9.3)	30.4 (5.7)
22	0.1	17.4 (9.9)	13.2 (4.0)	12.9 (9.8)	17.5 (3.2)	41.5 (3.4)	21.1 (2.8)
44	0.2	0.0 (1.4)	16.1 (3.7)	17.6 (5.4)	15.5 (3.7)	37.6 (3.8)	22.3 (4.5)
88	0.4	0.3 (0.1)	0.0 (2.4)	0.4 (0.9)	0.5 (0.1)	32.3 (5.8)	10.4 (3.4)
176	0.8	0.7 (0.3)	0.0 (0.3)	0.0 (0.3)	0.5 (0.2)	2.0 (1.7)	2.7 (1.1)
220	1.0	0.3 (0.1)	0.0 (0.3)	0.0 (0.0)	0.4 (0.3)	0.9 (0.3)	1.1 (0.6)

The purpose of the third part of the research was to estimate remedial efficacy of boron compounds. Therefore fungal infested specimens were exposed to six wood decay fungi for 6 weeks. During this period of exposure wood specimens lost between 8.5% (*A. vallantii*) and 24.3% (*G. trabeum*), indicating that all fungi used were vital. There was very interesting phenomenon observed, that infested specimens retained considerable higher amounts of aqueous solutions than observed at control-uninfested specimens. The highest uptakes were observed at specimens partially decayed by *H. fragiforme* (400 kg/m^3), and the lowest at spruce wood blocks decayed by *G. trabeum* (50 kg/m^3) (Table 3). This fact should be taken into consideration, when interpreting obtained results. In order to inhibit growth of the fungi, that have already colonized wood specimens, considerably higher boron concentrations were required. For most of the fungi 5000 ppm of B in preservative solution was required to inhibit their growth on the wood, while for some of the most resistant (*S. lacrymans*, *A. vaillantii*) even the highest concentration of 8700 ppm of B was necessary to prevent them (Table 4).

Table 3: Retention of boric acid (BA) into Norway spruce and beech specimens. Specimens were exposed to wood-decaying fungi for 7 weeks.

Fungal species	Wood species	Uptake of solution	Boron concentration (ppm)				
			0	1000	2500	5000	8700
		kg/m^3	Retention of BA	Retention of BA	Retention of BA	Retention of BA	Retention of BA
Antrodia vaillantii	Spruce	78.9	0	0.08	0.20	0.40	0.68
Gloeophyllum trabeum		49.8	0	0.05	0.12	0.22	0.43
Serpula lacrymans		128.6	0	0.13	0.32	0.64	1.12
Pleurotus ostreatus	Beech	89.8	0	0.09	0.22	0.45	0.78
Trametes versicolor		272.4	0	0.27	0.68	1.36	2.37
Hypoxylon fragiforme		401	0	0.40	1.00	2.00	3.49

Table 4: Influence of immersion of fungal colonised specimens to boron based aqueous solution of various concentrations on fungal growth. Fungal growth was estimated visually, with marks between 0 (complete retardation of fungal growth at all specimens) and 3 (fungal mycelia grew from all infested specimens)

Fungal species	Boron concentration (ppm)				
	0	1000	2500	5000	8700
	Fungal growth (0 – complete retardation; 3 – no retardation)				
Antrodia vaillantii	3	3	2	1	1
Gloeophyllum trabeum	3	3	0	0	0
Serpula lacrymans	3	3	1	1	0
Pleurotus ostreatus	3	3	2	0	0
Trametes versicolor	3	3	1	0	0
Hypoxylon fragiforme	3	3	2	0	0

In comparison to the copper, boron compounds were found considerably more effective. Aqueous solution of 10.000 ppm of Cu was not sufficient to inhibit growth of most of the fungi, with exemption of *P. ostreatus.*

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