EFFICACY OF TANNIN IN FIXING BORON IN WOOD: FUNGAL AND TERMITE RESISTANCE

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The easy leaching of boron from wood preservation formulations has limited the use of this highly active fungicide. The recently discovered adduct with flavonoids allows boron to be retained for longer periods of time within wood and consequently to extend its life. Two different leaching treatments were compared, and the fungal and termite decay were examined. The biological tests showed extremely high resistance of the leached samples against both fungus (*Coriolus Versicolor* and *Coniophora Puteana*) and termites (*Reticulitermes Santonensis*). The retention of 2.5 kg/m³ was determined as the threshold of efficacy of boron in flavonoid-based wood preservative. Furthermore, solid state ^{13}C-NMR analysis of the tannin resin indicated that boron can be covalently fixed to the tannin-hexamine network.

INTRODUCTION

For more than fifty years boron-based formulations for wood preservatives have been presented to the scientific community (Findlay 1960) and up to now many research groups have worked in this field.

Simple borates such as boric acid, borax, or disodium octaborate tetrahydrate (DOT) are wide spectrum wood preservatives (Lloyd 1997; Drysdale 1994), which could be of interest for industrial applications, as their odourless, colourless, and non-flammable characteristics can be combined into a relatively inexpensive product. These borates are also soluble in water allowing them to be introduced in wood by conventional methods such as dipping-diffusion or vacuum-pressure treatments (Byrne and Morris 1997; Lebow and Morrell 1989).

Boron compounds have been shown to have low human toxicity (Teshima *et al.* 2001; Usuda *et al.* 1998; Jansen *et al.* 1984), and boric acid has been considered environmentally acceptable for many years.

On the other hand, this high water solubility makes boron compounds easily leachable from treated wood and thus boron-treated wood is not suitable for outdoor applications (Lloyd 1998; Peylo and Willeitner 1997). The key issue to expand the use of boron for wood protection appears to be their fixation into wood, while at the same time

allowing sufficient mobility to maintain their fungicidal characteristics (Obanda *et al.* 2008).

Over the years there have been various tests with boron formulations and other chemicals in order to improve the durability of wood preservative treatment (Van der Drift and La Brijn 1988; Gezer et al. 1999; Kartal et al. 2004) but the problem of high leachability of boron has not yet been completely solved.

A significant break-through in the development of this technology was the discovery of the interaction of boron compounds with tannins (Pizzi and Beacker 1996).

The anchorage of boron with flavonoid tannins was proposed in the following years (Thevenon et al. 1998), and up to now many studies have been carried out to define the properties of these innovative formulations. New tannin-boron formulations in alkaline environment have been recently investigated (Thevenon et al. 2009). These formulations showed significant results, and they were further studied to extend their protection properties to softwoods (Tondi et al. 2012a) and to their possible applications in outdoor buildings (Tondi et al. 2012b).

In this paper various modifications of the tannin-boron based formulations were studied, with particular attention being paid to the following aspects:

- The restrained leaching of boron due to tannins by comparing two methods of leaching

- The biocide effects of several innovative formulations

- The chemical investigation through solid state ^{13}C-NMR on the tannin-hexamine cross-linked networks

EXPERIMENTAL

Material

Beech (*Fagus sylvatica*) and Scots pine (*Pinus Sylvestris*) wood specimens of $50 \times 25 \times 15$ mm^3 (length, width, thickness) were treated with a number of experimental wood preservatives. These solutions were prepared with the following products: Mimosa (*Acacia Mearnsii* formerly *mollissima*, de Wildt) tannin extract provided by Silva (Italy); Hexamethylentetramine (Hexamine), boric acid, phosphoric acid and ammonium hydrogen phosphate supplied by Lactan. In addition, 1-methyl-2-propanol and sodium hydroxide were provided by Sigma-Aldrich.

Preparation of the Impregnation Solutions

The tannin powder was dissolved in a mechanically stirred water solution of boric acid. 6% of hexamine and the other additives (1-methyl-2-propanol, H_3PO_4, $(NH_4)_2HPO_4$) were added before adjusting the pH of the solution to the value of 9.0 with a 50% solution of NaOH. The exact series of applied treatment is reported in Table 1. The tannin and the other formulation components are expressed in relation to the total composition of the resin (w./w.).

Table 1. Description of Water-Based Tannin-Boron Formulations

Tannin (w/w %)	Boric acid (w/w %)	1-Methyl-2-propanol (w/w %)	Other Additives (w/w %)
10	0.5	1	
15	0.75	1	
20	1	1	
20	1		
20	0.6	1	
20	1.4	1	
20	1	1	1% of H_3PO_4
20	1	1	1% of $(NH_3)_2HPO_4$

Impregnation Process

The wood specimens, prepared according to EN113, were dried for at least three days at 104°C and placed into a desiccator where an 8 mbar vacuum was applied for 30 minutes to remove the majority of the trapped air inside the wood cells. The desiccator was then filled with the impregnation solution, and the pressure was slowly increased to environmental pressure.

Depending on the different types of wood treated and the viscosity of the impregnation solution, various impregnation times (2 to 24 hours) were applied. The impregnated samples were cleaned with blotting paper and kept for 12 hours at 104°C to allow for the hardening of the tannin-hexamine resin. Subsequently, the impregnated specimens were stored in a climatic chamber for at least one week at 20°C and 65% RH. The retention levels were calculated using the weight of the samples before and after the impregnation process.

Leaching Methods

Ten of the treated specimens were used for each leaching method.

Daily exchange for five days

Two series of five specimens were leached in 500 mL of water (wood: water = 1: 5.3 v/v) at 20 °C. The water was changed daily for five days. 50 mL of the exhausted water was collected to determine the concentration of boron through ICP-OES analysis.

Once the samples were air dried, the anhydrous weight of the samples (dried at 103 °C) was recorded after the treatment and after the leaching. At the end of the leaching cycle the samples were air dried and stored for at least one week at 20°C and 65%RH before being tested for their biocide properties against fungus and termites.

EN-1250 leaching

Two series of five specimens were leached with 500 mL of stirred water according to the guideline of EN 1250-2 (1995). The water was exchanged at the following leaching times: 1, 2, 4, 8, 16, and 48 hours. 50 mL of exhausted water was collected to determine the amount of boron through ICP-MS analysis. At the end of the leaching cycle the samples were air dried and stored for at least one week at 20°C and 65%RH before being tested for their biocide properties against fungus and termites.

The two leaching methods were applied to evaluate the effect of leaching. One involved an experimental period of 5 days, as in our previous research work (Thevenon et al. 2010). The other was according to the European standard.

ICP-OES: Boron Determination

The aqueous leachate from the treated samples was analysed by Inductively Coupled Plasma- Optical Emission Spectrometry (ICP-OES) to determine the concentration of boron released during the leaching process. This analysis was performed in a ICP Varian equipped with CCD (Coupled Charge Device) using the wavelength 249.7 nm.

Biological Attacks

Test against fungus

The treated specimens were tested to evaluate their resistance against biological attack according to the guidelines specified in EN113 (1996). In order to obtain discriminant results, the samples of beech were exposed to *Coriolus versicolor* (strain CTB 863), whereas the Scots pine samples were tested against *Coniophora Puteana* (strain BAM 15).

The specimens were selected for fungal attack and grown on a malt/agar medium (malt 40, agar 20 g/L). All wood samples were sterilized by gamma radiation. In each culture flask, one treated specimen and a control (untreated Beech or Scots pine) were inserted.

Virulence controls were also performed on twenty specimens of beech and twenty specimens of Scots pine, and the samples were exposed to 22 °C, 65% m.c. for 16 weeks.

Once the fungal exposure was completed, the mycelium was removed and the specimens were weighed in order to evaluate their humidity at the end of the fungal exposure. The specimens were then dried at 103 °C, and their final weight was recorded. The humidity at the end of the test (data not shown) as well as the weight loss of the control were determined with strict adherence to EN113.

Tests against termites

Scots pine treated and untreated samples were exposed to termites (*Reticulitermes Santonensis*) in no-choice feeding tests according to EN117 (2005) guidelines.

Each specimen was placed at the bottom of a glass cylindrical bottle blocked at one end with dental plastone to form a strong 5 mm barrier. 250 termite workers, 5 soldiers, and 5 nymphs were collected and placed with each specimen. The samples were kept at 26°C and 70% relative humidity for eight weeks.

By the end of the test, most of the termites had died. The weight loss of the wood sample was the parameter selected to quantify the efficacy of the wood preservative.

Solid State ^{13}C-NMR Analysis

Two solutions of tannin-hexamine (40% solid content) were prepared with and without 10% of boric acid respectively, and their pH was adjusted to 9.0. The two beakers were then stored at 103°C for 12 hours. The cured resins were crushed with a mortar, and the powders were analysed with solid state ^{13}C-NMR.

The spectrum was obtained on a Brucker MSL 300 FT-NMR spectrometer at a frequency of 75.47 MHz and at a spin sample of 4.0 kHz. The duration of the impulse at 90° was 4.2 ms, the contact time was 1 ms, the number of transients was approx. 1000, and the decoupling field was 59.5 kHz. As a control, the chemical shifts were determined in relation to tetramethylsilane.

RESULTS AND DISCUSSION

Retention Results

Every water-borne formulation used in wood preservation science is sensitive to the leaching action of the water. Hence, the tannin-hexamine networks are also affected by this phenomenon and the quantification of its leachability is fundamental for the industrialization process of these formulations. For this reason the retention levels of leaching for tannin and boric acid are reported in the following table:

Table 2. Retention of Tannin and Boric Acid before and after Leaching

Wood Species	Treatment	Retention before leaching (kg/m³)			Retention after leaching - 5 days - (kg/m³)		
		Tannin	Boric Acid	Standard deviation*	Tannin	Boric Acid	Standard deviation*
Beech	10% Tan.+ 0.5% H_3BO_3	57.61	2.88	1.3	44.79	2.24	1.6
Beech	15% Tan.+ 0.75% H_3BO_3	98.61	4.93	2.3	80.72	4.04	2.1
Beech	20% Tan.+ 1.0% H_3BO_3	128.25	6.41	2.8	108.49	5.42	2.8
Beech	20% Tan.+ 1.0 % H_3BO_3 No Solv.	130.61	6.53	2.9	110.86	5.54	3.0
Beech	20% Tan.+ 0.6 % H_3BO_3	133.40	4.00	1.9	114.57	3.44	3.0
Beech	20% Tan.+ 1.4 % H_3BO_3	130.89	9.16	3.7	105.81	7.41	3.8
Beech	20% Tan.+ 1.0 % H_3BO_3+ 1.0 % H3PO4	125.01	6.25	5.2	96.38	4.82	5.2
Beech	20% Tan.+ 1.0 % H_3BO_3 + 1.0 % (NH4)2HPO4	89.07	4.45	8.7	69.09	3.45	7.6
S.Pine	10% Tan.+ 0.5% H_3BO_3	65.01	3.25	1.6	47.41	2.37	1.6
S.Pine	15% Tan.+ 0.75% H_3BO_3	97.71	4.89	10.5	73.74	3.69	9.1
S.Pine	20% Tan.+ 1.0% H_3BO_3	109.34	5.47	9.8	84.93	4.25	8.8
S.Pine	20% Tan.+ 1.0 % H_3BO_3 No Solv.	130.64	6.53	7.3	105.13	5.26	6.7
S.Pine	20% Tan.+ 0.6 % H_3BO_3	107.58	3.23	12.3	84.00	2.52	13.8
S.Pine	20% Tan.+ 1.4 % H_3BO_3	136.73	9.57	4.3	105.84	7.41	3.1
S.Pine	20% Tan.+ 1.0 % H_3BO_3+ 1.0 % H3PO4	124.04	6.20	8.9	90.67	4.53	8.4
S.Pine	20% Tan.+ 1.0 % H_3BO_3 + 1.0 % (NH4)2HPO4	125.01	6.25	5.3	96.38	4.82	4.6

* Standard deviation calculated on the total taken up

The biologically active component in these wood preservatives is boron. In each formulation, less than 10 kg/m³ of boric acid was applied, which in terms of active element boron is between 0.5 and 1.7 kg/m³ of boron. These retention levels are comparable to those currently used by other research groups: a) in the field of boron preservatives (Kartal and Green 2003; Lyon et al. 2007); b) and in the field of heavy-metal preservatives (Green and Clausen 2005; Rathigan et al. 2004; Zelinka et al. 2010).

Leaching Behaviour

The behaviour of tannin-boron wood preservatives is reported in Figs. 1 and 2. In these graphics the boron released during the leaching was quantified through ICP-OES.
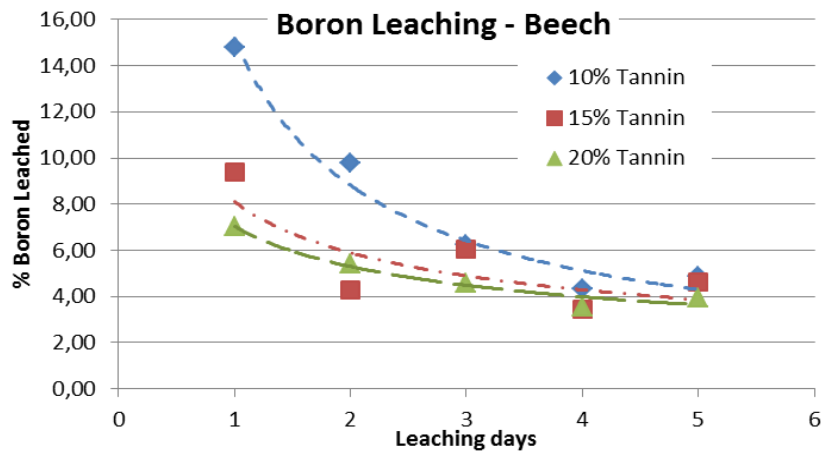

Fig. 1. Percentage of boron released by tannin-boron treated beech samples monitored every day for the 5 days of leaching
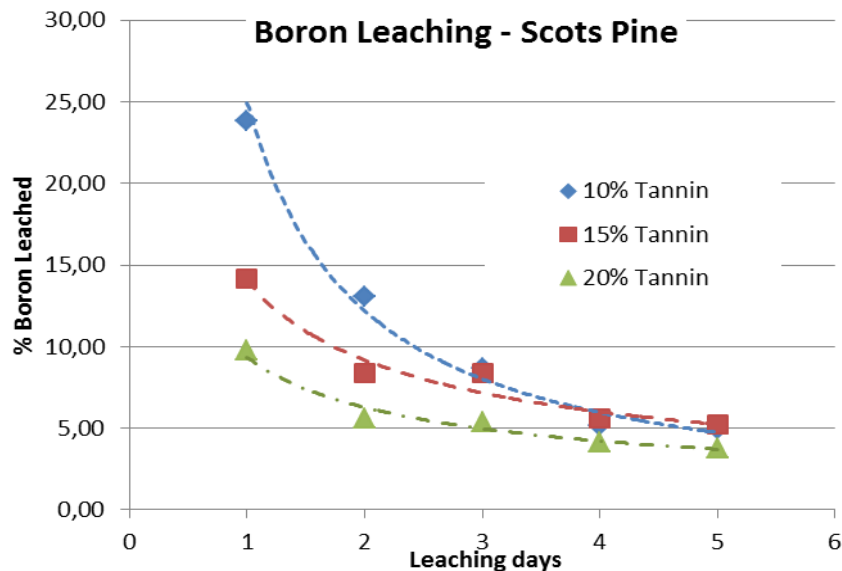

Fig. 2. Percentage of boron released by tannin-boron treated Scots pine samples monitored every day for the 5 days of leaching

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These two figures show clearly that the boron is leached out mainly at the beginning of the leaching process. This phenomenon can be explained based on an incomplete polymerization of the tannin resin. Indeed, the solutions of the first washings were always brownish due to the solubilisation of low-molecular weight tannin which also contains some fixed boron.

These flavonoid oligomers and the free boric acid will be the first to be leached out. This also occurs in the subsequent leaching but with a decisive decrease in intensity.

The leaching was more evident when a lower concentration of tannin was applied. The greater the content of tannin found in the wood structure, the easier it would be to create a high molecular weight reticule, consequently reducing the amount of leached-out boron.

This effect was observed for both the studied species, Scots pine and European beech. In the case of beech, much less material was leached out because the polymer can easily crosslink between the vessels. The crosslinking of the tannin into the narrow morphology of the tracheids of Scots pine produces thin layers that can leach out with greater ease.

Moreover, the lower longitudinal penetration of Scots pine (Scholz et al. 2010) does not allow a perfect distribution of the impregnating solution, and the solid preservative is mainly stored in the surface tracheids. This less homogeneous distribution impedes the correct polymerization of the flavonoids and produces lower molecular weight oligomers that are also easy to leach.

The leaching tests were also evaluated according to the European Norm 1250-2, and the results are reported in Fig. 3.
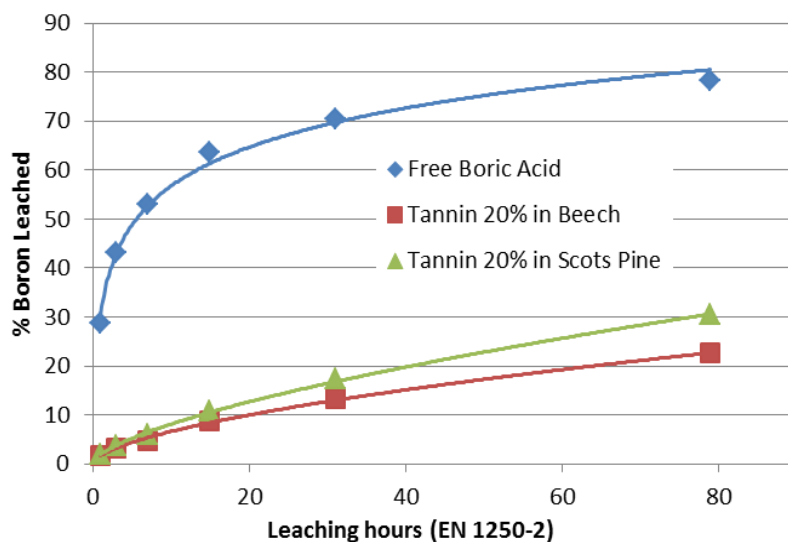

Fig. 3. Boron leached out during the EN-1250 leaching test for a 10 g/L boron solution. Free and with 20% tannin for European beech and Scots pine

This graphic makes clear the point that the leaching of boron occurs much slowly when it is fixed with tannin solutions. The tendency of the curve of free boron showed a greater loss of boron which decreased due to the fact that there was almost no more boron available (More than 50% of boron was leached out in the first 7 hours). When boron was

fixed with tannin, there was only 30% loss of material at the end of the completed leaching cycle, and the trend shows that the loss of material will always be smaller.

When comparing the two leaching methods (Fig. 4), it can be observed that at the end of the cycle the two methods were really similar: The EN 1250-2 method is just slightly more vigorous for pine treated samples, while the 5-day leaching affects the beech samples more. This effect is logical: If it is more difficult for tannin resin to penetrate Scots pine, then most of the polymer network will then be located on the surface of such samples. The stirring system applied in the EN 1250-2 method will put more stress on the surface; hence, the Scots pine samples will be the ones more affected by this kind of leaching.
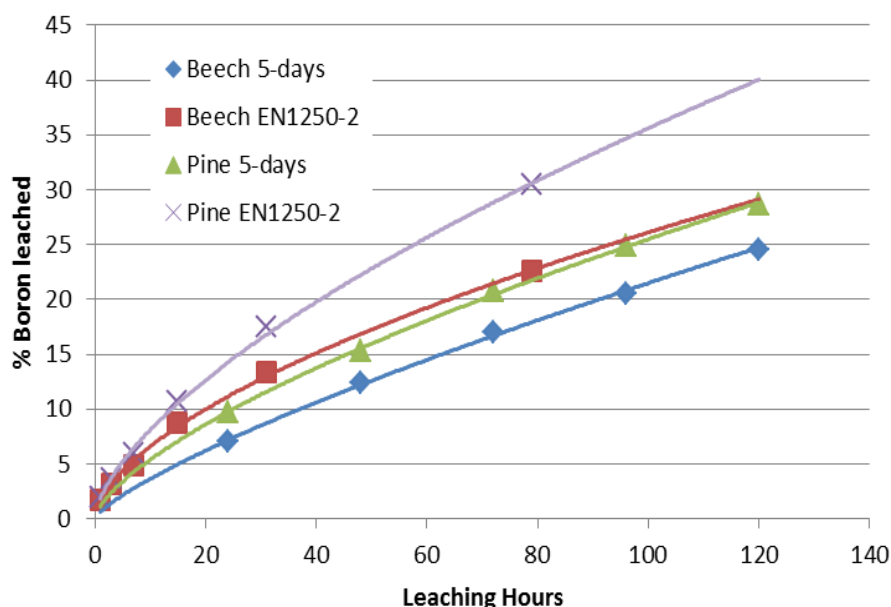

Fig. 4. Boron leached from Beech and Scots pine samples treated with 20% tannin-boron formulations: Comparison of leaching efficacy between 5-day method and EN1250-2 methods

The two analysed methods were shown not to be exhaustive for the leaching of the fixed boron, since both methods were able to leach just 30% of the originally penetrated boron. The tendency of the curves showed a continuous decrease in leaching, but was not possible to foresee if this loss of boron would continue.

On the other hand, the test indicated that the boron was fixed by the tannin resin. Indeed, after 80 hours of leaching less than 30% of boron had been leached out. Nevertheless, it would be interesting to evaluate the leaching behaviour for longer leaching periods in more extensive studies.

Biological Tests Findings

Table 3 lists the biological activity for the results regarding the weight loss of each treatment. The columns defined as W.L. describe the weight loss due to the fungus *C. Puteana*" as well as "*C. Versicolor*" and the termites "*R. Santonensis*".

Table 3. Results of the Biological Attacks for all the Tannin-Boron Formulations *

Wood	Tannin %	H_3BO_3 %	Leaching	Modification	W.L.(*CP*) %	Ref. %	W.L.(*CV*) %	Ref. %	W.L. Termites	Ref. %
Beech	10	0.5	5-days				2.1 (2.2)	32.8		
Beech	15	0.75	5-days				0.6 (0.3)	26.8		
Beech	20	1	5-days				1.6 (0.3)	50.3		
Beech	20	1	not leached				1.1 (0.7)	30.7		
Beech	20	1	5-days	No solvent			0 (0.1)	31.9		
Beech	20	0.6	5-days				1 (0.3)	34.6		
Beech	20	4.1	5-days				0.5 (0.3)	34.1		
Beech	20	1	5-days	1% H_3PO_4			0.4 (0.2)	31.4		
Beech	20	1	5-days	1% $(NH_4)_2HPO_4$			1.9 (0.9)	37.4		
S.Pine	10	0.5	5-days		3.2 (2.4)	44.1			3.5 (0.3)	8.1
S.Pine	15	0.75	5-days		0.8 (0.2)	46.0			1.4 (0.3)	8.1
S.Pine	20	1	5-days		0.9 (0.7)	50.3			1.0 (0.2)	8.1
S.Pine	20	1	not leached		0.1 (0.1)	26.7			2.4 (0.4)	8.1
S.Pine	20	1	5-days	No solvent	1.1 (0.6)	40.1			1.5 (0.2)	8.1
S.Pine	20	0.6	5-days		2.6 (1.9)	41.2			2.3 (0.5)	8.1
S.Pine	20	4.1	5-days		0.7 (0.3)	43.4			1.0 (0.3)	8.1
S.Pine	20	1	5-days	1% H_3PO_4	0.3 (0.3)	44.9			1.4 (0.4)	8.1
S.Pine	20	1	5-days	1% $(NH_4)_2HPO_4$	2.2 (4.2)	47.2			4.3 (1.0)	8.1
S.Pine	20	1	EN1250		0.4 (0.3)	46.2			1.5 (0.1)	8.1
S.Pine		25 g/L	EN1250		0.1 (0.1)	41.5			1.3 (0.1)	8.1
S.Pine		25 g/L	not leached		0.3 (0.1)	27.2			0.7 (0.1)	8.1

* The European beech samples were tested against *C. versicolor*, whereas those belonging to Scots pine were tested against *C. puteana* and *R. santonensis*.

This series of data has to be carefully interpreted: according to EN113 and EN117, all the tests in which the weight loss is less than 3.0% have to be considered successful. Therefore, only two failed tests were found: Pine samples treated with 10% tannin against *C. Puteana* and termites; and pine treated with ammonium hydrogen phosphate against termites. In all the other cases the formulations achieved the test specifications.

In the case of the test for Scots pine sample treated with 10% tannin, the failure was predictable. This is because the combined effect of the extremely low boron content (0.5%) and low degree of polymerization of tannins in Scots pine treated samples leads to an inevitable failure.

The boron retention of this formulation before leaching was 3.25 kg/m³, and after leaching only around 2.37 kg/m³ remained. However, the high activity of this biocide means that a satisfactory treatment can be achieved even if only a small loss in weight is reached, which is also the case for extremely low concentrations. Eventually, only 3.5% of the mass of the samples was attacked by termites and only 3.18% was attacked by the *C. puteana*.

Table 3 indicates that the ammonium hydrogen phosphate also has weak biocide properties. Indeed, all the results were worse than the homologue formulations with phosphoric acid. In addition, the ammonium can be assimilated by the basidiomycetes (Mikes et al. 1994), hence this formulation was abandoned.

A definitive aspect of the investigation was the determination of the minimal amount of boron required. The tests have shown that satisfactory results can also be obtained with 0.6% of boric acid but with a stronger polymeric network (20% of tannin in

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the formulation). In this case the retention level of boron was 3.23 kg/m³, which was reduced to around 2.52 kg/m³ after 5-day leaching. It is possible to assert that the value of 2.5 kg/m³ is the minimal concentration of boron required to reach the standard according to EN113 and to EN117. The amount of 0.6% is more than eight times lower than the boron allowed by law in wood preservation formulations (EC 1998/8).

For all the other formulations the results were even more satisfying, for example solvent free (1-methyl-2-propanol-free) and phosphoric acid modified formulations even improved preservation properties against fungus and termites (Figs. 5 through 7).

Fig. 5. Biological attack of *C. Puteana* on tannin-boron treated *(left)* and untreated *(right)* Beech specimens

Fig.6. Biological attack of *C. Versicolor* on untreated *(left)* and tannin-boron treated *(right)* Scots pine specimens

a)

b)

Fig.7. Biological attack of *R. Santonensis*: a) Untreated and b) tannin-boron treated samples

^{13}C-NMR Analysis of the Polymer

Tannin-hexamine polymers are condensation products constituted by oligomers of flavonoids interconnected with aliphatic bridges, the latter of which may also include amino groups (Fig. 8). The intermediate stage in this reaction includes the formation of reactive imines (Pichelin et al. 1999)
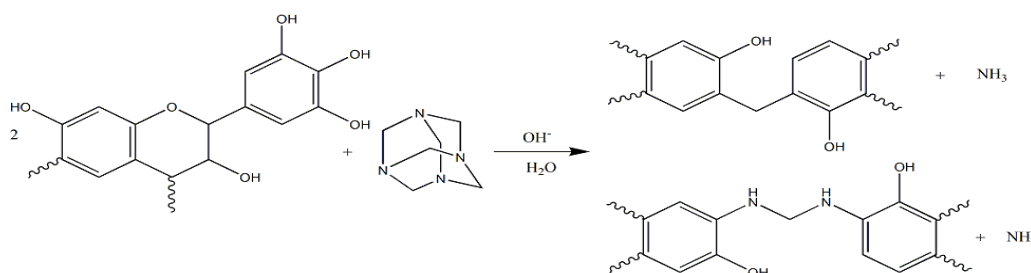

Fig. 8. Chemical mechanism hypothesis relating to the tannin-hexamine condensation

The effect of boron in this condensation seems to be really effective because of the high differences noticed in the ^{13}C-NMR spectra (Fig. 9).
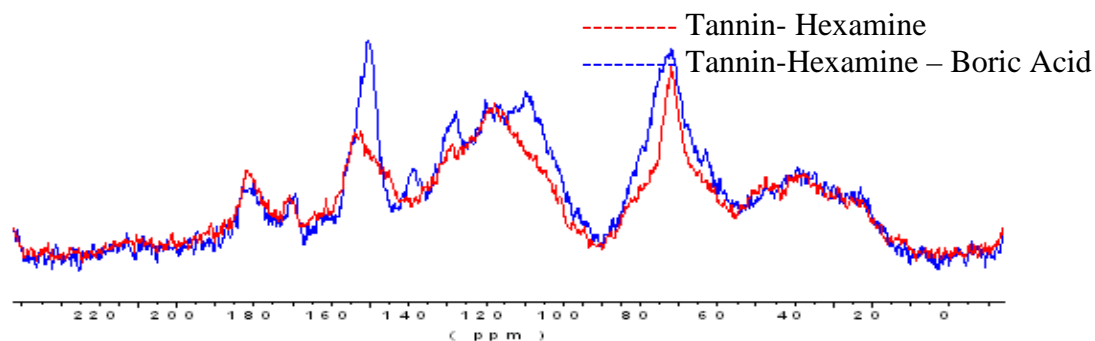

Fig.9. ^{13}C-NMR spectra of tannin-hexamine networks with and without boric acid

The main differences between the spectra of the two polymers are reported in Table 4, in which the assignment of the values was carried out according to the literature (Pizzi, 1994; Cambridgesoft 1998).

Table 4. Interpretation of the Differences between the Two Spectra of Tannin Hexamine Networks with and without Boric Acid

Signal (ppm)	Description	Meaning
181	Carboxylic acids	Slightly more carboxyl acids found. Boric acid can contribute.
153	• C-O-R groups in 5,7,9 of the A-ring of the flavonoid. • Aromatic C in etherocycles with 2 oxygens and boron (Fig.10)	• More hydroxy groups are etherified. • The etherification can involve boron connected with phenol-like structure.
138	• C-O Benzofurane • Aromatic C in etherocycles with 2 oxygens and boron (Fig.10)	• Boron catalyzes furan-like rearrangements. • Pentatomic ring constituted by 2 vicinal –OH both etherified by boron
129	Connection Ring A-B	The reorganization produces more ring to ring connections.
110	Interflavonoid connection	Boron catalyzes the polymerization.
75	Alifatic C in etherocycles with 2 oxygens and boron	Pentatomic cycles of boron.
64	Alifatic ring carbons of mono-substitute –OH (ring-O-B) (Fig.10)	Boron-oxygen-aliphatic bond

The stronger improvement of the signal at 153 ppm is the most important effect of boric acid behaviour in the crosslinking phenomenon.

The presence of boron catalyses the etherification of the hydroxyl groups of the flavonoid. This means that boric acid can be active in the etherification of these hydroxyl

groups or that it activates the etherifications with other groups of the system (amines, imines of fragments of other flavonoids).

The simultaneous improvement of the signal at 138, 75, and 64 ppm confirms that boric acid participates actively in the networking reaction because these signals can be attributed to boron adducts similar to those reported in Fig. 10 .
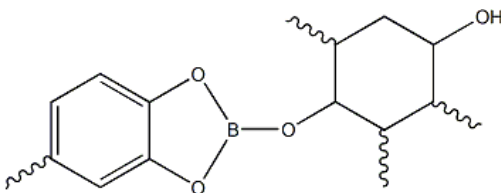

Fig. 10. Possible adduct between two flavonoids with aromatic and aliphatic parts connected by single or cyclic ether bonds

The three hydroxyl groups of boric acid can be mono-, di-, or completely substituted. Figure 10 only shows the case in which three hydroxyl groups are etherified, but in terms of biological activity it is more probable that at least one of the three branches of boric acid maintains the free –OH group.

The signals at 129 and 110 ppm indicate that tannins catalysed by boron produced more cycle-to-cycle connections, explaining the increase of the polymerization degree (Pizzi 1994).

It is highly possible that the boric ethers catalyse the polymerization process also directly participating (three branches etherified). The reaction is driven by a mechanism in which oxygen-containing cycles are favoured and the presence of heterocyclic compounds including boron is also highly possible. The information extrapolated by the ICP-MS analysis is, therefore, confirmed by the solid state ^{13}C-NMR spectra of the tannin-hexamine polymers: Boron is fixed by the tannin network.

CONCLUSIONS

Three main tasks were accomplished in this article: demonstration of the leachability of tannin-boron formulations, the efficacy of the leached product, and the chemical explanation of the previous two tasks. Water leaching is a key-factor in the development of tannin-boron, long-term, water-borne wood preservatives.

Very encouraging results were achieved in the leaching process: Tannin-based preservatives lose less than 30% of boron after one complete leaching cycle instead of the 80% loss by the tannin-free formulations. However, the study of the behaviour for longer leaching periods will be necessary for the further development of these formulations.

High biocide activity was determined. The tannin-boron wood preservatives showed that they can easily exceed the European standard required for water leachability. The main information achieved for the improvement of the formulation is as follows:
- The threshold value of 2.5 kg/m³ for boron efficacy was determined.
- The use of phosphoric acid does not compromise the efficacy of the formulation.

- Ammonium salts have to be avoided.
- High-performing formulations can be set up without necessitating the use of solvents.

The compatibility between phosphoric acid and the formulation opens the door for a wood preservative that can also be applied in fireproofing solutions.

Artificial and natural weathering test with long cycles of exposure are necessary to confirm the efficacy of these formulations.

The ^{13}C-NMR chemical study has clarified the role of boric acid in the formation of the tannin-hexamine network. Boron has been found to be covalently connected to the flavonoid network and to be a catalyst for the polymerization between condensed tannin molecules. Penta-atomic structures including boron and oxygen are highly possible.

This study has contributed to an understanding of the anchorage mechanism of boron and could lead to more extensive research on this extremely active biocide as a long-term wood preservative.

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