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**Wood protecting chemicals**

**Tannin resin-boron associations:  
Leaching and biological resistance**

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# Tannin resin-boron associations: Leaching and biological resistance

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## ABSTRACT

The easy leaching of boron in wood preservation formulations has allowed to use this fungicide only for short term applications. The recently discovered adduct with flavonoids allows boron to resist longer periods of time within wood and consequently extend its life.

Two different leaching treatments were compared and the fungal and termite decay was examined. The biological tests have shown extremely high resistance of the leached samples against both, fungus (*Coriolus versicolor* and *Coniophora puteana*). The resistance towards termites (*Reticulitermes flavipes* ex. *santonensis*) was also evaluated. A threshold concentration for the efficacy of boron as wood preservative was determined. Furthermore, the solid state <sup>13</sup>C-NMR analysis of the tannin resin has permitted to prove the anchorage of boron to flavonoids.

**Keywords:** tannin preservatives; leaching resistance; boron fixation; termites; fungus; <sup>13</sup>C-NMR analysis

## 1. INTRODUCTION

For more than fifty years, the boron-based formulations for wood preservatives have been well known to the scientific community (Findlay, 1960). During the following decades, various formulations were proposed, but the high leaching problems of boron compounds was the main reason why these low-toxicity compounds were commercialized only for short-term applications (Van der Drift and La Brijn, 1988; Turner, 1981).

Borates such as boric acid, borax or disodium octaborate tetrahydrate (DOT) have proved their efficiency for many years as wide spectrum wood preservatives (Lloyd 1997, Drysdale 1994). They have many advantages including being inexpensive, odourless, colourless and non-flammable. They 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 proven to have a 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, yet they allow sufficient mobility to maintain their fungicidal characteristics (Obanda et al. 2008).

A significant break-through on the development of this technology was achieved with 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 done to define the properties of these innovative formulations. New tannin-boron formulations in alkaline environment have been recently proposed (Thevenon et al. 2009). These formulations showed significant results and were further studied to extend the protection properties of softwoods (Tondi et al. 2012a) and for their possible applications in outdoor buildings (Tondi et al. 2012b).

In this paper various modifications of the tannin-boron based formulations are studied and particular attention was emphasised on the following aspects:

- The restrained leaching of boron due to tannins by comparing two methods of leaching.
- The biocide effects of several innovative formulations are also reported.
- The chemical investigation through solid state  $^{13}\text{C}$ -NMR on the tannin-hexamine crosslinked networks.

All these tests have contributed to understand the anchorage mechanism of boron and to reconsider this extremely active biocide as long-term wood preservative.

## 2. EXPERIMENTAL METHODS

### 2.1 Material

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

### 2.2 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,  $\text{H}_3\text{PO}_4$ ,  $(\text{NH}_4)_2\text{HPO}_4$ ) were added before adjusting the pH of the solution at the value of 9.0 with a 50% solution of NaOH.

The exact series of applied treatment is reported in Table 1.

The percentage of tannin is reported in relation to the total composition of the resin (w./w.) while the other components of the formulation are referred to the amount of tannin (w./w.)

Table 1: Formulations

Series	Tannin (w/w <sub>sol</sub> %)	Boric acid (w/w <sub>tan</sub> %)	1-Methyl-2- propanol (w/w <sub>tan</sub> %)	Other Additives (w/w <sub>tan</sub> %)
A	10	5	5	
B	15	5	5	
C	20	5	5	
D	20	5		
E	20	3	5	
F	20	7	5	
G	20	5	5	1% of H <sub>3</sub> PO <sub>4</sub>
H	20	5	5	1% of (NH <sub>3</sub> ) <sub>2</sub> HPO <sub>4</sub>

### 2.3 Impregnation

The wood specimens, prepared according to the guidelines of EN113, were dried for at least three days at 103°C and placed into a desiccator where 8 mbar vacuum was applied for 30 minutes to remove the majority of the trapped air inside the wood cells. Then, the desiccator was filled up 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 103°C to allow the hardening of the tannin-hexamine resin.

Then, the impregnated specimens were stored in a climatic chamber for at least one week at 20°C and 65% RH

### 2.4 Leaching

Ten of the treated specimens were used for each batch leached with both methods.

#### 2.4.1 Daily exchange for five days

Two series of five specimens were leached in 500 ml of water (grade 3) (ratio wood/water = 1/5.3 v/v) at 20 °C. The water was changed daily for five days. 50 ml of the exhausted water were 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 resistance against fungi and termites.

#### 2.4.2 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 with the following leaching times: 1, 2, 4, 8, 16 and 48 hours. 50 ml of exhausted water were 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 biologically tested.

## 2.5 ICP-OES boron determination

The leaching water of the treated samples were analysed by Inductively Coupled Plasma- Optical Emission Spectrometry (ICP-OES) to determine the concentration of boron released during the leaching process. These analysis were done in a ICP Varian equipped with CCD (Coupled Charge Device) at the wavelength 249.7 nm.

## 2.6 Biological efficacy

### 2.6.1 Tests towards Basidiomycete fungi

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

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

Six replicates were tested for each impregnation solution. Along, 4 replicates were tested on non-inoculated malt-agar media. These samples are correction coefficient and will be use to correct the test samples weight loss. Virulence controls were also performed on twenty specimens of both beech and Scots pine sapwood. All samples were exposed for 16 weeks at 22°C, 65% RH. Once the fungal exposure was finished, the mycelium was removed from the wood blocks and the specimens were weighed in order to determine 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 and corrected weight loss (using the correction coefficient) of each specimen were determined according to the EN113.

### 2.6.2 Tests against termites

Treated and untreated Scots pine sapwood samples were exposed to termites (*Reticulitermes santonensis*) in a no-choice feeding tests according to the guidelines of EN117 (2005).

Each specimen was placed in a test device with 250 termite workers, 5 soldiers and 5 nymphs. Three specimens for each impregnation batch, as well as controls were kept at 27°C and 70% relative humidity for eight weeks.

At the end of the test, the samples are removed and the survival rate of the termite workers is calculated. Each sample is given a visual rating (data not shown), but the weight loss of the wood sample was the selected parameter to quantify the efficacy of the wood preservatives (as nor boron or tannins are repellent active ingredients).

## 2.7 Solid state <sup>13</sup>C-NMR analysis

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

The spectrum was obtained on a Bruker 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 about 1000 and the decoupling field was 59.5 kHz. As a control, the chemical shifts were determined in relation to tetramethylsilane.

### 3. RESULTS AND DISCUSSION

#### 3.1 Leaching

The retentions of the different batches are given in table 2.

Table 2: Retentions

Treatment	Beech			Pine		
	Retention before leaching kg/m <sup>3</sup>			Retention before leaching kg/m <sup>3</sup>		
	Tannin	Boric acid	Std dev*	Tannin	Boric acid	Std dev*
10% tannin + 0.5% Boric acid	57.61	2.88	1.3	65.01	3.25	1.6
15% tannin + 0.75% Boric acid	98.61	4.93	2.3	97.71	4.89	10.5
20% tannin + 1% Boric acid	128.25	6.41	2.8	109.34	5.47	9.8
20% tannin + 1% Boric acid No solv.	130.61	6.53	2.9	130.64	6.53	7.3
20% tannin + 0.6% Boric acid	133.40	4.00	1.9	107.58	3.23	12.3
20% tannin + 1.4% Boric acid	130.89	9.16	3.7	136.73	9.57	4.3
20% tannin + 1% Boric acid +1% H <sub>3</sub> PO <sub>4</sub>	125.01	6.25	5.2	124.04	6.20	8.9
20% tannin + 1% Boric acid + 1% (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	89.07	4.45	8.7	125.01	6.25	5.3

\*standard deviation calculated on the total taken up

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

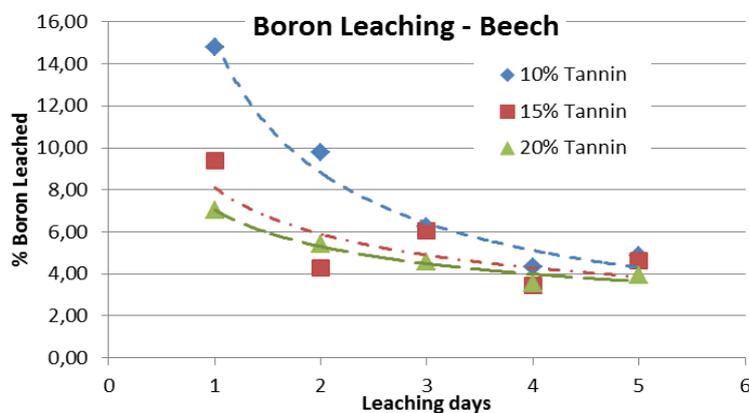


Figure1: Percentage of boron released by tannin-boron treated beech samples monitored every day for the 5 days leaching.

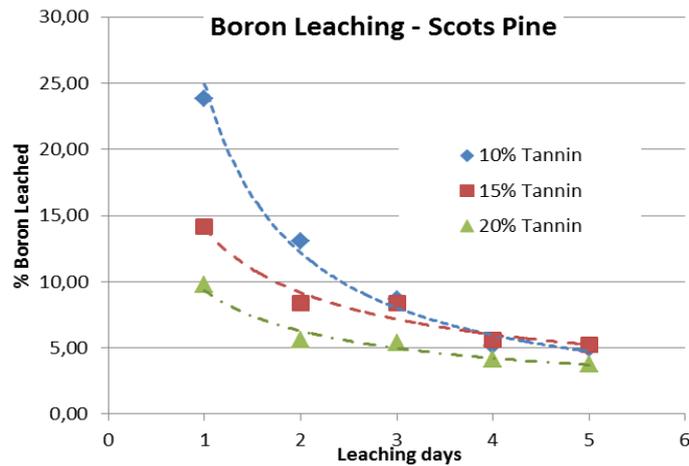


Figure 2: Percentage of boron released by tannin-boron treated Scots pine samples monitored every day for the 5 days leaching.

These two figures show clearly that the boron is leached out mainly at the beginning of the leaching process. This phenomenon can be explained with an incomplete polymerization of the tannin resin. Indeed, the solutions of the firsts washing are always brownish due to the solubilisation of low-molecular weight tannin which contains also some fixed boron. These flavonoid oligomers and the free boric acid will be the first to be leached out. This mechanism occurs also in the following leaching but with a decisive decreasing of intensity.

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

This effect was observed for both the studied species: Scots pine and beech. In the case of beech much less material was leached out because the polymer can easily crosslink between the vessels. The cross-linking 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 Figure 3.

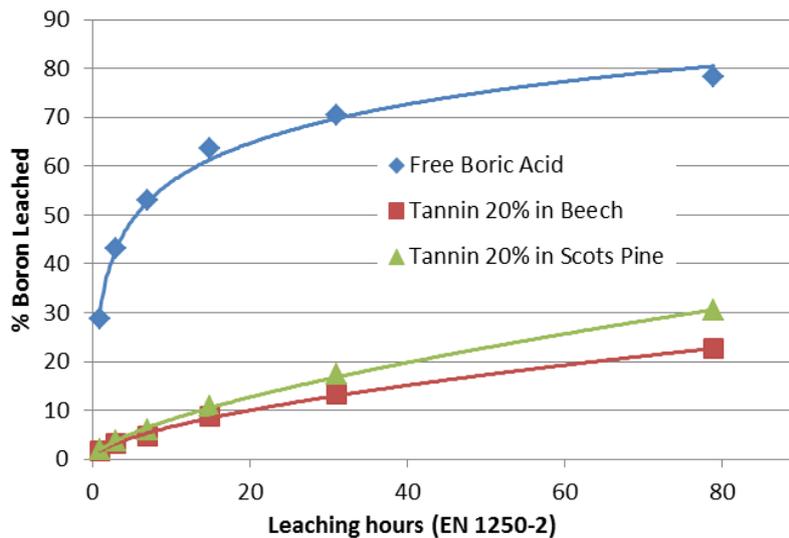


Figure 3. Boron leached out during the EN-1250 leaching test for a 10 g/L boron solution, free and fixed with 20% tannin for beech and Scots pine.

This graphic underlines 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 there was almost no more boron available (more than 50% of boron is leached out in the first 7 hours). When boron is fixed with tannin there is 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 are rather similar: EN 1250-2 method is just slightly more vigorous for pine treated samples, while the 5-days leaching affect more the beech samples.

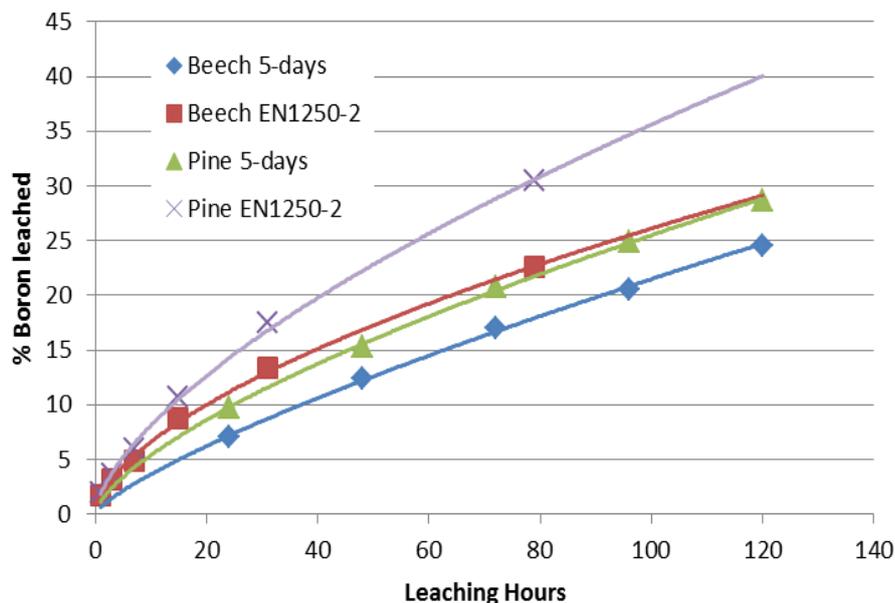


Figure 4: Boron leached from beech and Scots pine samples treated with 20% tannin-boron formulations: Comparison of leaching efficacy between 5-days and EN1250-2 methods.

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 shows that there is a continuous decrease of the leaching but is not possible to foreseen if this loss of boron will be completed. However the fixation of boron takes place because after 80 hours of continuous contact with water less than 30% of boron is leached out.

### 3.2 Biological resistance

The biological tests results are reported in table 3.

The termite tests were performed according to the EN117. As an active ingredient, boric acid is not repellent, meaning that the termites have to degrade some treated wood before being eradicated. Thus, we chose to compare the results obtained on a weight loss basis and arbitrary decided that a mean mass loss below 3% reflects an efficient treatment and that the termiticidal threshold is reached (these criteria being the one for the Japanese Industrial Standard K 1571 (JIS 2004)).

Table 3: Results of the biological test against Basidiomycete *Coniophora puteana* (CP), *Coriolus versicolor* (CV) and termites

Wood	Treatment			Leaching	Weight loss (CP) %	Control weight loss %	Weight loss (CV) %	Control weight loss %	Weight loss (termites) %	Termite control weight loss %
	Tannin %	Boric acid %	Other							
Pine: CP Termites  Beech: CV	10	0.5		5-days	3.2 (2.4)	44.1	2.1 (2.2)	32.8	3.5 (0.3)	8.1
	15	0.75		5-days	0.8 (0.2)	46.0	0.6 (0.3)	26.8	1.4 (0.3)	
	20	1		5-days	0.9 (0.7)	50.3	1.6 (0.3)	50.3	1.0 (0.2)	
	20	1		unleached	0.1 (0.1)	26.7	1.1 (0.7)	30.7	2.4 (0.4)	
	20	1	No solvent	5-days	1.1 (0.6)	40.1	0 (0.1)	31.9	1.5 (0.2)	
	20	0.6		5-days	2.6 (1.9)	41.2	1.0 (0.3)	34.6	2.3 (0.5)	
	20	4.1		5-days	0.7 (0.3)	43.4	0.5 (0.3)	34.1	1.0 (0.3)	
	20	1	1% H <sub>3</sub> PO <sub>4</sub>	5-days	0.3 (0.3)	44.9	0.4 (0.2)	31.4	1.4 (0.4)	
	20	1	1% (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	5-days	2.2 (4.2)	47.2	1.9 (0.9)	37.4	4.3 (1.0)	
	20	1		EN1250	0.4 (0.3)	46.2			1.5 (0.1)	
	25g/L		Un-leached	0.3 (0.1)	27.2			0.7 (0.1)		
(standard deviation)										

This series of data have to be carefully interpreted: according to EN113 and EN117, all the tests in which the mean corrected weight loss is less than 3.0% (and only 1 sample with a correct weight loss between 3 and 5%) have to be considered successful. Therefore, only one failing test has been found: Pine samples treated with 10% tannin against *Coniophora puteana*.

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 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/m<sup>3</sup>; and after leaching only around 2.37 kg/m<sup>3</sup> remained.

Table 3 indicates that the ammonium hydrogen phosphate, a well recognized fire retardant, 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.

In this configuration, 2 formulations only have shown their non-efficacy towards termites: Pine samples treated with 10% tannin and Pine treated with ammonium hydrogen phosphate.

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% tannin formulation). In this case the retention level of boron was 3.23 kg/m<sup>3</sup>, which was reduced to around 2.52 kg/m<sup>3</sup> after 5-days leaching. It is possible to assert that the value of 2.5 kg/m<sup>3</sup> is the minimal concentration of boron required to reach the standard according to EN113 and EN117/JIS K 1571. The amount of 0.6% is 8 times lower than the boron allowed by the European directive 2008/58/EC in wood preservation formulations.

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 the biological resistance.

### 3.3 <sup>13</sup>C-NMR analysis of the polymer

Tannin-hexamine polymers are condensation products made of oligomers of flavonoids interconnected with aliphatic bridges, the latter of which may also include amino groups. The intermediate stage in this reaction includes the formation of active imines (Pichelin et al., 1999). In our case, the effect of boron in this condensation seem to be really effective as there was a high difference in the solid state <sup>13</sup>C-NMR spectra of the tannin-hexamine polymers. (Fig.5)

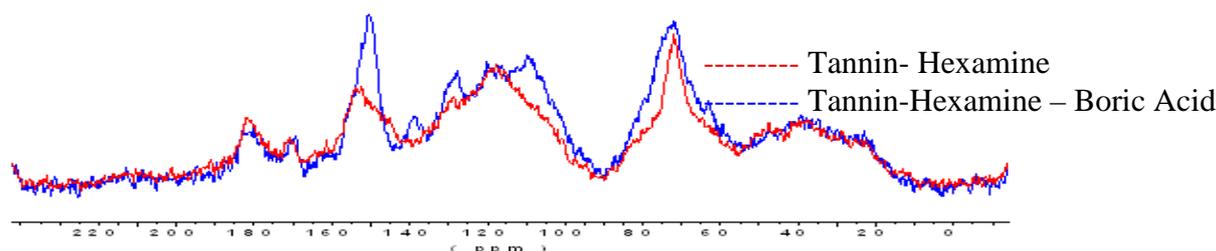


Figure 5: <sup>13</sup>C-NMR spectra of tannin-hexamine networks with and without boric acid.

The main differences between the spectra of the two polymers are reported in table 4 (Pizzi, 1994 ; Cambridgesoft, 1998).

The stronger improvement of the signal at 153 ppm is the most important effect of boric acid behaviour in the crosslinking phenomenon. In an alkaline medium the rearrangement of the tannins occurs easily with the opening of the C2 from the A-ring of flavonoids (Pizzi, 1994). The presence of boron drives the rearrangement to cycles which contain oxygen.

The improvement of the signal at 64, 75 and 138 ppm confirms this reaction. According to this, boron can be included in the new rearrangements producing pentatomic cycles with the following molecular formula. The signals at 129 and 110 ppm clearly state that the molecular network of tannins catalyzed by boron produces more cycle-to-cycle connections explaining the increase of the polymerization degree. The reaction is driven by a mechanism in which oxygen-containing-cycles are favoured. The presence of heterocyclic compounds including boron is also highly possible. The slight increasing of the signal at 181 ppm shows only the increasing amount of acid oxygen available (due to H<sub>3</sub>BO<sub>3</sub>). The information extrapolated by the ICP Analysis is,

therefore, confirmed by the solid state  $^{13}\text{C}$ -NMR spectra of the tannin-hexamine polymers : boron is fixed by the tannin network (Tondi et al, 2012)

Table 4: Interpretation of the difference 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 group in 5,7 and 9 of the A-ring	More alcohol groups are etherified.
138	C-O Benzofurane	Boron catalyzes furanic rearrangements.
129	Connection Ring A-B	The reorganization produces more ring to ring connections.
110	Interflavonoid connection	Boron catalyzes the polymerization.
75	C-O-B structures	Boron coordinations.
64	Alifatic C in etherocycles	Pentatomic coordination of Boron. with 2 oxygens

#### 4. CONCLUSION

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

Very encouraging results have been achieved for leaching: tannin based preservatives loose around 10% of boron instead of the 80% for tannin-free formulations, leading thus to high biological performances. However, the study of the behaviour for longer leaching period will be necessary for the further development of these formulations.

The  $^{13}\text{C}$ -NMR chemical study has clarified the role of boron in the formation of the tannin-hexamine boron. Boron has been found to be a good catalyst for the rearrangement of the flavonoid molecules. The major amount of boron is complexed through secondary bonds with the rearranged flavonoid structure, but smaller parts of boron can also be fixed with covalent bonds in pentatomic structures.

It also has to be underline that for further developments, the compatibility between phosphoric acid and the formulation opened the door for a wood preservative with fireproof solution.

#### 5. ACKNOWLEDGEMENTS

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