# DURABILITY OF TANNIN-BORON-TREATED TIMBER

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Tannin-boron wood preservatives were investigated for their resistance against outdoor agents. This work focused on the analysis of the causes that affect the durability of the tannin-hexamine-treated samples. In particular, dimensional stability, resistance to leaching, and resistance to biological agents were investigated. The combined effect of deterioration agents was evaluated by subjecting the treated samples to simulated and natural weathering tests. The study of the appearance and of the color components (*L**, *a**, and *b**) according to CIELAB space of the exposed samples was monitored to assess the efficacy of the tannin-boron formulations for outdoor applications. Significant resistance against the action of water (EN 84, ENV 1250-2) and insects (EN 47) has been demonstrated in specific tests. Conversely, the continuous stress due to artificial and natural weathering deteriorates the color and the visible features of the treated specimens. The combined effect of moisture modifications, solar exposition, and leaching cycles damages the structure of the tannin-based polymeric network and subsequently it negatively affects its preservation properties.

*Keywords: Tannin; Colour measurement; Weathering; Dimensional stability; Insects; Leaching*

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## INTRODUCTION

Even though the ECHA committee has recently classified boric acid as a "substance of very high concern" (2010), boron-based wood preservatives for outdoor applications are one of the most attractive topics in wood preservation (Peylo and Willeitner 1995; Obanda *et al.* 2008). The high biocide activity of boron has been well studied. Very low concentrations of this element are lethal for most fungi and insects (Drysdale 1994; Lesar and Humar 2009). Boron-based preservatives have high water solubility. This facilitates the use boron in waterborne formulation but at the same time it represents the principal drawback after application (Baysal and Yalinkilic 2005; Kose *et al.* 2011). Indeed, free-boron based formulations, such as boric acid and octaborates, are highly active immediately after treatment, but very weak after a limited time of outdoor exposure. For this reason some formulations have been developed to try to anchor boron in timber, but most of the time such efforts destroy the biocidal activity of boron (Peylo 2005; Kartal and Green 2003).

High performing results in this area have recently been found for formulations based on tannin-boron adduct (Thevenon *et al.* 2009): Leached tannin-boron treated samples lost less than 2% of mass after 16 weeks exposure against *Pycnoporous sanguineus* under tropical conditions. These results have been explained in recent

investigations, where it has been demonstrated that tannins are able to chemically fix boron without affecting its biocide activity (Tondi *et al.* 2012a). These tannin-boron formulations were also tested for applications under conditions for which high mechanical and fireproof properties were required (Tondi *et al.* 2012b).

The positive outcomes of the previous tests have led the research group to study the tannin-boron formulations from two perspectives: First, their behavior toward single deterioration agents was studied, and then the combination of the agents was investigated. In the first part, the following aspects were analysed:

- Leaching resistance according to EN 84 (1997) and ENV 1250-2 (1995);
- Resistance to *Hylotrupes bajulus* according to EN 47 (2005);
- Dimensional stability of the treated samples under different humidity conditions;

The information gained through these preliminary tests allowed a better comprehension of the weathering behavior of these wood preservatives that were investigated through color measurements.

## EXPERIMENTAL

### Materials

Scots pine (*Pinus sylvestris* L.) boards consisting mainly of sapwood from different Austrian sawmills were selected and stored in a climate chamber (20 °C, 65% RH). The samples were successively cut in different dimensions, and the heartwood regions and knots were discarded. Mimosa (*Acacia mearnsii*) bark extract was provided by Silva Chimica, while the chemicals were delivered by Lactan. Solutions of 5% boric acid, 33% hexamethylenetetramine (hexamine), and 50% NaOH were prepared using deionized water (% w/w).

### Methods

*Impregnation*

Scots pine sapwood specimens were dried at 103 °C until constant mass was reached. These samples were successively placed into a desiccator in which an 8 mbar vacuum was applied for 30 minutes. The desiccator was then filled with the impregnation solution, and the pressure was slowly increased up to ambient pressure (Thevenon *et al.* 2010). The specimens were kept in the tannin-based solution for 24 hours before being removed and were then lightly wiped with blotting paper. The weights of the samples were monitored at the end of the impregnation process to obtain a batch which was as homogeneous as possible.

The wet samples were kept for at least 12 hours at 103 °C to allow the tannin-based resin to harden. Subsequently the treated specimens were stored in a climatic chamber (20 °C, 65% RH). Tannin impregnation solutions were prepared with 10% and 20% w/w mimosa extract. The pH of these solutions was always corrected with NaOH 50% to a pH of 9.0. Then 6.0% of hexamine (w/w tannin) and 5.0% (w/w tannin) of boric acid were added at the end of the preparation.

*Leaching methods*

Ten impregnated samples with dimensions of 50 x 25 x 15 $mm^3$ (L, R, T) were leached strictly according to the two normative methods: EN 84 and ENV 1250-2. The EN 84 leaching method involves a preliminary vacuum-pressure impregnation of the

treated samples with water and 12 following water exchange in a period of 15 days immersion, while the ENV 1250-2 leaching method is a more dynamic method in which the treated samples are immersed in constantly stirred water for 1, 2, 4, 8, 16, and 48 hours. The leaching waters of both tests were collected for the evaluation of the tannin loss. The amount of tannin dissolved in the leaching waters was analysed in absorption with a Merck spectroquant Nova 60 visible spectrometer at a 340 nm wavelength. The concentration ($C$) of the tannin solutions was extrapolated applying experimental calibration lines $C = (Abs_{340nm} - 0.0785)/ 0.0013$, with $R^2 = 0.9902$.

*Insect tests*

Insect tests were carried out according to the EN 47 standard method for determination of toxic values of biocides against larvae of *Hylotrupes bajulus*. Five samples with dimensions of 50 x 25 x 15 $mm^3$ were selected for each formulation. Six holes, approximately 3 mm deep, were made in a diagonal pattern on the upper longitudinal face of each test sample. A newly hatched larva of *Hylotrupes bajulus* was carefully inserted head first into each hole. After exposure to the larvae, test specimens were put on a filter paper dish in single jars and placed in a controlled chamber at 22 °C and 70% RH for 4 weeks.

After exposure, each sample was examined by means of X-ray analysis to determine the amount of larvae which had survived.

*Dimensional stability*

Three series of Scots pine consisting of ten specimens, each having dimensions of 20 x 20 x 10 $mm^3$ (R, T, L), were selected to undergo dimensional stability tests. Untreated, 10% tannin-treated, and 20% tannin-treated Scots pine specimens were monitored to evaluate their behaviour under various moisture conditions. The three dimensions and the weight of the samples were first registered in an anhydrous state (0% humidity) for 1 week followed by exposure to 30%, 65%, and 85% relative humidity at 20 °C.

*Artificial and natural weathering*

Series of 5 samples of treated and untreated Scots pine of dimensions 150 x 75 x 20 $mm^3$ (L, T, R) were exposed to artificial and natural weathering. The simulated weathering was carried out in a QUV/spray accelerated weathering tester (Q-Panel Lab Products Cleveland, USA) according to the guidelines of EN 927-6 (2006). The exposure cycle started with a condensation phase (24 hours), followed by short intervals of UV-light (2.5 hours) with UVA-430 lamps and water spray (0.5 hour). The duration of the artificial weathering test was 955 hours.

The natural weathering test included fixing the untreated and the tannin-treated specimens in a 45° grid located in Kuchl (Austria) and exposing them toward the south for 158 days of weathering. The evaluation of the colour of the samples were carried out approximately every 50 days.

The wood colour was measured with a Mercury 2000 spectrophotometer (Datacolor). The diameter of the spotlight used for measurement was 11 mm. The wood colour was determined according to the CIELAB space with CIE standard illuminants D65 and a 10° standard observer. The CIELAB colour space was characterized by three parameters $L^*$, $a^*$, and $b^*$. The $L^*$ parameter represents the lightness, for which the value

of $L^*$ ranges from 0 (black) to 100 (white). The $a^*$ and $b^*$ axis describe the chromatic coordinates on the green/red ($a^*$) and blue/yellow ($b^*$) axis.

Colour coordinates before, during, and after exposure were measured, resulting in nine measurements per sample and according to DIN 5033 (1979). The total colour difference $\Delta E^*$ was used to denote distinction between the initial colour and colour after the artificial and natural weathering tests.

## RESULTS AND DISCUSSION

The weathering process is a complex series of stresses that are exerted on every wood specimen exposed to outdoor conditions. In this research, single parameters such as leaching and biological resistance and dimensional stability were considered, and the effect of the artificial and natural weathering on color modification was evaluated.

### Leaching Properties

Water is one of the main causes of deterioration of wood preservatives, particularly for the boron-based formulations. For this reason, this parameter was investigated according to two normative leaching tests: EN 84 and ENV 1250-2.

*EN 84:* This leaching procedure was performed for the 10% and 20% tannin-treated wood specimens, and the trend is shown in Fig. 1.

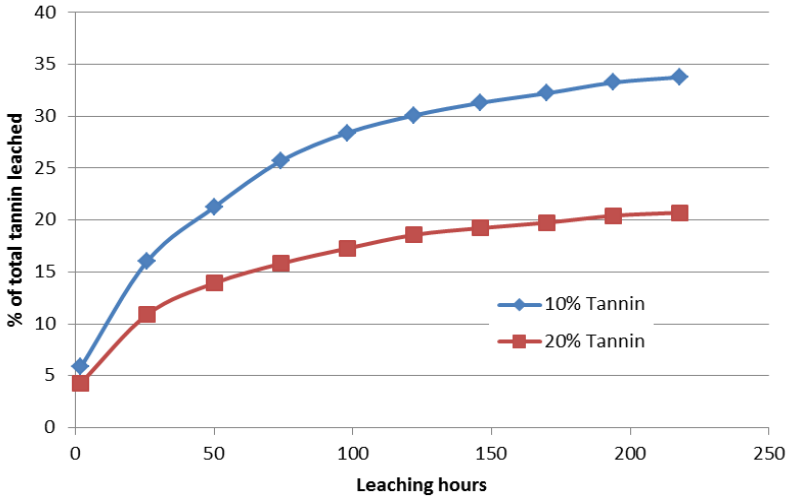


**Fig. 1.** Amount of tannin leached out of 10% and 20% treated samples according to EN 84

The amount of tannin that leached out with this method was quite high. The sample treated with only 10% tannin solution lost more than that treated with the 15% solution after only 24 hours of leaching. This high loss in the first part of the leaching also continued slowly in the final part. All in all, this treatment could leach out up to approximately 35% of the original tannin (and consequently boron) that was originally retained. The amount of tannin polymer that remained was still considerable, especially when more concentrated solutions were infiltrated. In the case of 20% tannin solutions, only around 20% of the tannin was leached out, so the amount of tannin was still sufficient to fix boron.

The method EN 84 is, indeed, a very aggressive leaching method. Nevertheless, in Europe, this leaching procedure represents the standard aging methodology prior to any biological resistance test for wood exposed in use classes 3 and 4 (outdoor exposure, above ground, and in-ground contact, EN 335 (2006)). This method strongly affects the network of the polymer located in the wood skeleton for two reasons. The first is that during the vacuum phase, the air trapped in the polymer network and in the wood cells exerts strains on the network. The second is that during the pressure phase, the water molecules almost completely replace the air that was trapped in the holes and exert a strong stress on the polymer; in this second phase, the molecules that were not polymerized are leached out and some of the most rigid polymer chains can break due to the swelling of wood. Moreover, with this method the contact surface between water and the polymer is highly increased and the leaching is much more effective.

*ENV 1250-2:* In Fig. 2, the trend of tannin lost according to the ENV 1250-2 method is represented.

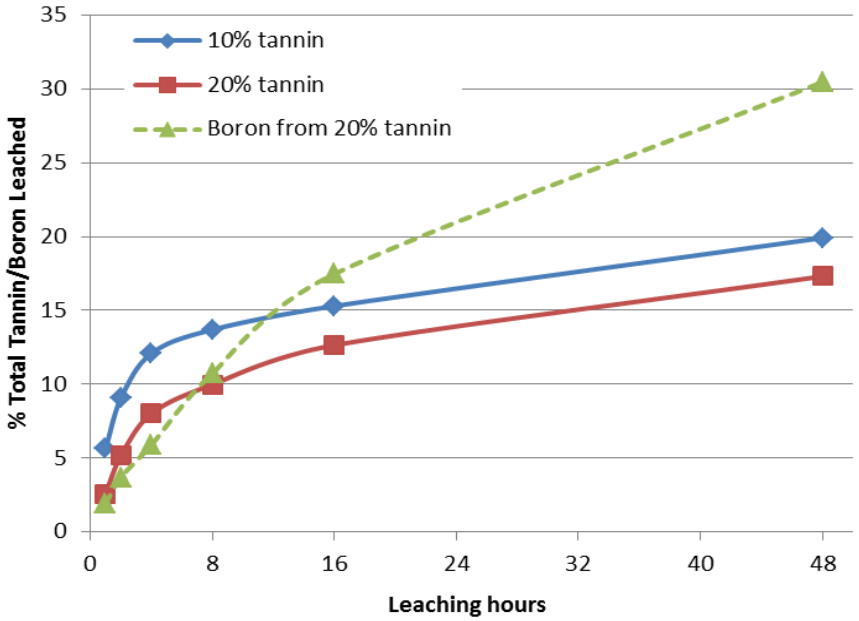


**Fig. 2.** Amount of tannin leached out of 10% and 20% treated samples and amount of boron leached out from 20% tannin-boron treated samples according to ENV 1250-2

The amount of tannin leached indicated two trends. At the beginning, the unreacted tannin at the surface was easily leached out. The flow then decreased but without showing the trend of being complete. This means that the water penetrated into the inner layer of the specimens and leached out all the unreacted fractions. In this case, the polymeric network was not destroyed by water; only the unreacted molecules were leached out (less then 20% of the initial amount). It is interesting to see that this trend is very similar to the one of boron analysed through ICP-MS (Tondi *et al.* 2012a) and reported in green dashes in Fig. 2. The only difference is the intensity of the loss. The cycle of ENV 1250-2 leached out around 30% of the boron and around 17% of the tannin. This means that some of the molecules of boron were: (i) not fixed to tannins or (ii) fixed to unreacted tannins. It can be noted that the tannin oligomers that are combined

with boron have less sites available for crosslinking; hence the possibility of them leaching out is higher.

This leaching procedure is milder than the EN 84, and it represents more realistically what happens during weathering because most of the leaching takes place on the surface and the water acts dynamically on it.

A further aspect that is underlined in both Figs. 1 and 2 is that low concentrated solutions of tannin do not have the ability to create stable networks, and many oligomers are still unreacted, being very susceptible to leaching out.

## Biological Properties

The resistance of the tannin-boron-treated samples against insects (unleached and leached) was evaluated. The main results are reported in the first column of Table 1.

**Table 1.** Biological Resistance of 20% Tannin-Treated Samples against Insects, Fungi, and Termites

| Formulation | Coleoptera (*Hylotrupes bajulus*) Survival rate (%) | Fungi, brown rot (*Coniophora puteana*) % Weight loss | Termites (*Reticulitermes santonensis*) % Weight loss |
|---|---|---|---|
| Untreated | 43 | 41.1 * | 8.1 * |
| 20% treated Unleached | 3.3 | 0.1 * | 2.4 * |
| 20% treated Leached ENV1250-2 | 10 | 0.4 * | 1.5 * |
| 20% treated Leached EN84 | 30 | - | - |

*= (Tondi *et al.*, 2012a)

The 20% tannin formulations were effective against insects to different extents. The unleached samples in particular showed an almost complete resistance to the larvae of *Hylotrupes bajulus*. In this experiment, the mortality rate of the reference control was lower than the validity test criteria (70% of untreated samples). This was probably due to the fact that the larvae were put in contact with wood two days after hatching. For this reason some larvae were weak and died prematurely. Nevertheless, the leached sample with ENV 1250-2 showed interesting results with a survival rate of only 10%. The test with larvae was not satisfactory when the samples were leached according to EN 84. This means that, according to the European standard, the wood preservative was not effective against insects even though the survival rate was 30% higher than for the untreated samples. The EN 84 procedure indeed breaks the polymer and further boron containing fragments are leached out, compromising the efficacy of the formulations against insects. For this reason, there was also little interest in running tests against brown rot fungi and termites. Although the leached specimens treated with 20% tannin solutions were not completely satisfactory against the *Hylotrupes bajulus*, there was a significant resistance to fungi and termites (Tondi *et al*. 2012a), which would encourage more attention to the real durability of the species undergoing simulated and natural weathering tests in which UV-rays and rain effects could be considered simultaneously.

## Dimensional Stability

Dry tannin-treated and untreated Scots pine samples were subjected to different moisture conditions in order to evaluate their swelling behavior. The radial and the tangential swellings are reported in Figs. 3 and 4. The behaviours of the 10% and 20% tannin-treated samples were very similar, and in particular the 20% samples indicate more accentuated swelling than the untreated ones. In the radial direction, the swelling was significant even with a low humidity level, while in the tangential direction notable differences in swelling takes place at only 85% relative humidity. During swelling, wood has the tendency to produce cracks. Polymers in the wood structure increase the swelling, which stresses the wood more and such treatment produces more or deeper cracks.

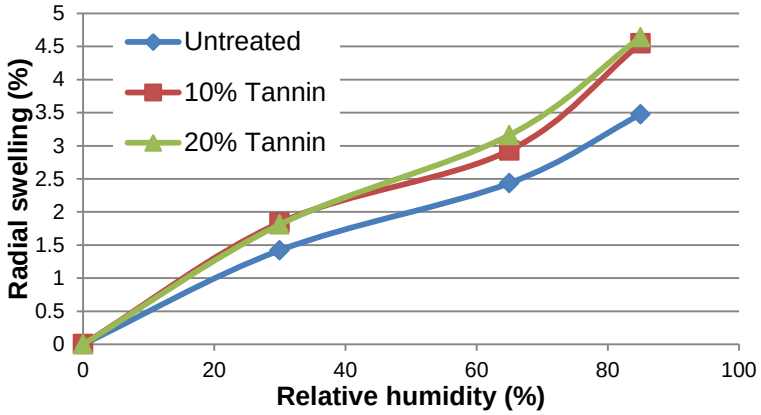


**Fig. 3.** Swelling behavior of untreated, 10%, and 20% tannin-treated samples: Radial direction

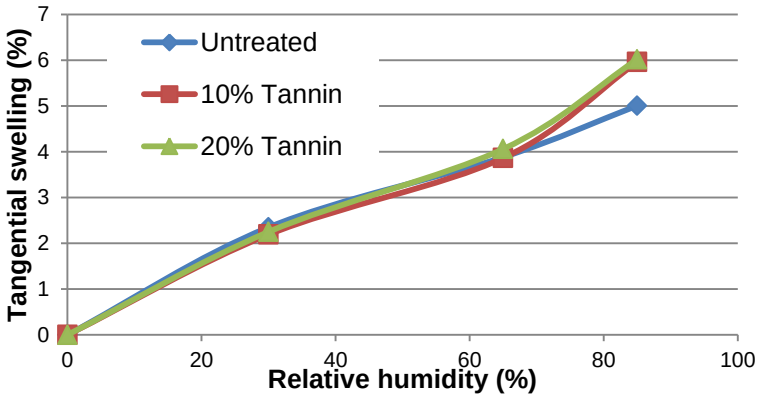


**Fig. 4.** Swelling behavior of untreated, 10%, and 20% tannin-treated samples: Tangential direction

The maximum internal stress was reached when the ratio between the radial and tangential swelling (swelling coefficient) was highest. From this viewpoint, it appears that for untreated wood this coefficient was always around 0.65, and for treated wood the ratio was around 0.75. This means that the internal strain of the treated sample was around 15% higher than the untreated ones. As a confirmation of this stress, the observation of the samples treated with 20% tannin solutions after natural weathering exposure showed deeper cracks than the untreated ones.

The more substantial increase of swelling in radial direction could be explained considering that most of the easy accessible cells for the tannin polymer during

impregnation are the latewood ones (Tondi *et al.* 2012c). Therefore the water molecule will be adsorbed more easily in the earlywood tracheids, driving the swelling mainly in the radial direction.

## Artificial Weathering

The color and the appearance of the samples during exposure were monitored during the exposure cycle of 955 hours. In order to obtain clearer information on the weathering discoloration, the behaviours of *L**, *a**, and *b** were investigated separately and are reported in Fig. 5.

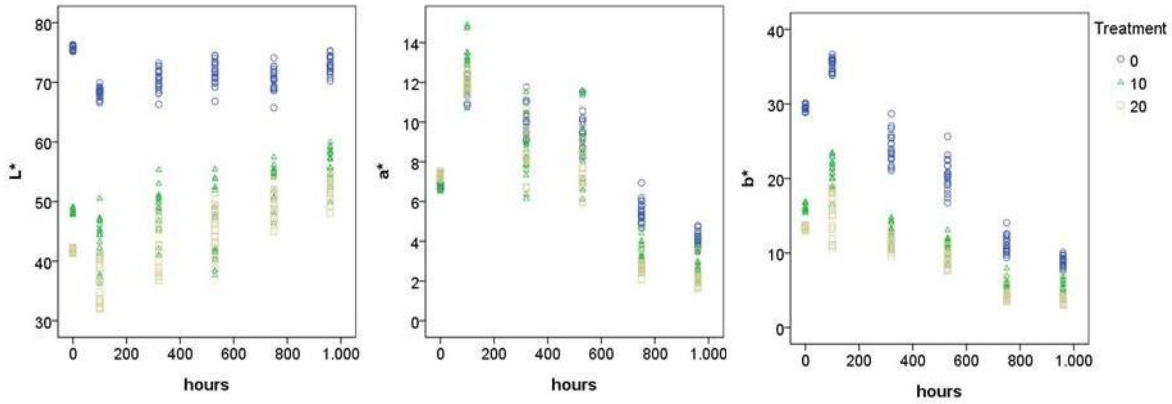


**Fig. 5.** Colour component (L*, a*, and b*) behaviour during the artificial weathering of untreated, 10%, and 20% tannin-treated specimens (0, 10, and 20, respectively).

The *L** value is the parameter that is associated with the brightness of the color. A low value of *L** corresponds to dark color. The trend of this parameter shows a strong decrease after 100 hours of exposure and then a very slight increase up to the end of the cycle even if the initial values were not achieved. This trend is in line with previous research (Temiz *et al.* 2007). The treated samples showed a slight decrease in *L** at the beginning of the weathering and after 100 hours, there was a strong and continuous increase until the end of the process. This trend shows that even if the treated samples were darker at the beginning of the process, the weathering discoloured the wood surface much faster. This greater increase in brightness that was observed for the treated samples is due not to the natural discoloration of the degraded lignin (Fengel and Wegener, 2003; Pandey, 2005; George *et al.* 2005), but mainly to the leaching of the tannin-based preservative that takes place to a high extent on the surface (Kataoka and Kiguchi 2001). The largest variation was observed at low concentrations, which confirms the trend observed during the leaching tests.

The *a** values increased during the first 100 hours, during which the colour of the samples shifted to reddish. The values then decreased considerably until the end of the weathering test (955 hours), as the intensity of the red colour faded for all wood samples. The *b** values of the untreated samples increased during the first 100 hours and the colour of the untreated samples shifted to a yellow tone resulting from the lignin degradation products (Müller *et al.* 2003). The values then fell slowly during exposure up to 955 hours. It can be assumed that a decrease in the *b** values during artificial weathering is related to the leaching of lignin and polyose products from the wood (Evans *et al.* 1992).

The same *b** values trend was observed for 10% and 20% treated specimens. However, the changes in the component *b** of the 20% treated samples were lower than the others even if at the end of the weathering test the yellow component in all the exposed samples were similar. This phenomenon is due to the preliminary loss of tannins and to the subsequent degradation of lignins and polyoses on the unprotected surface. The colour of all samples turned grey during the artificial weathering (Fig. 6). Significant differences between the untreated and tannin-treated samples were observed in the *L** values at the end of the exposure time. The *a** and b* values were similar for all samples.

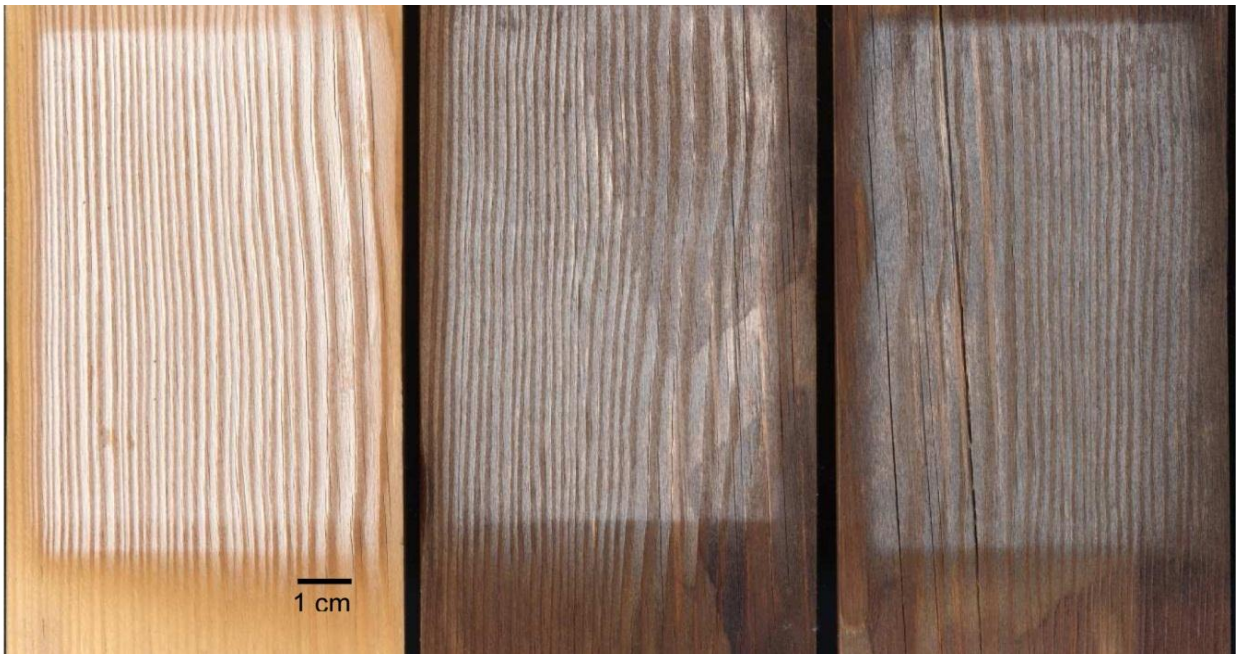


**Fig. 6.** Visible impression of changes in colour and cracks for untreated (left), 10% (middle), and 20% treated (right) samples weathered after 955 hours under artificial conditions

Some cracks were present on all the samples at the end of the cycle. The treated samples were subject to more frequent and deeper cracks and in particular, evident checks and splits were found in the 20% treated wood samples. This phenomenon is probably due to the higher swelling coefficient of the tannin-treated wood (Hansmann *et al.* 2006).

## Natural Weathering

The results of the discolouration during the artificial weathering were compared with the ones exposed to natural outdoor conditions (Fig. 7). Only the behaviour of the *L** values for untreated samples showed significant differences between natural and artificial weathering. In this case, indeed, the brightness of the colour decreased continuously.

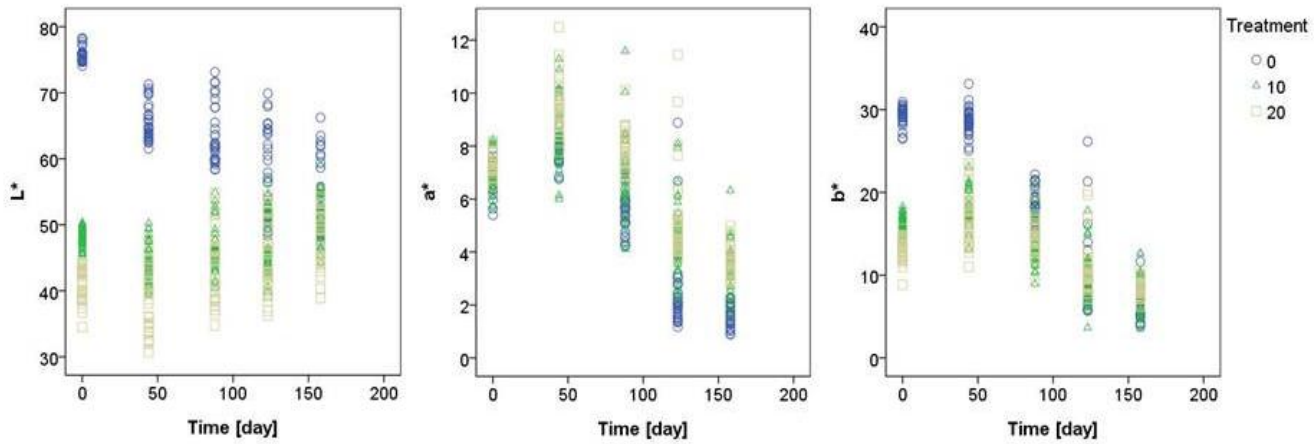


**Fig. 7.** Colour component (*L**, *a**, and *b**) behaviour during the natural weathering for untreated, 10%, and 20% tannin-treated specimens (0, 10, and 20, respectively)

The total colour difference Δ*E** shows that the colour of the tannin-impregnated samples was more stable regarding discoloration than the untreated pine samples (Fig. 8). One reason for this behaviour is the difference in initial colour; the treated samples showed significant differences in the *L** and *b** values compared to the untreated samples. The *L** values of the treated samples were, however, rather stable during the natural weathering test of 158 days.

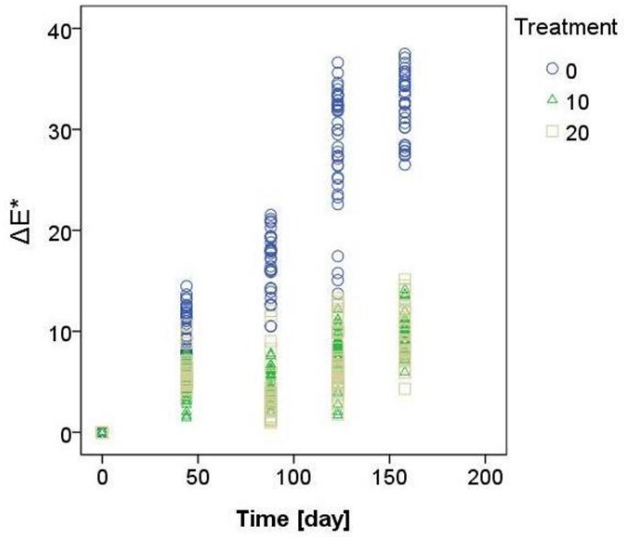


**Fig. 8.** Comparison of ΔE* colour during the natural weathering for untreated, 10%, and 20% tannin-treated specimens (0, 10, and 20, respectively)

The discoloration observed on the tannin-treated samples was less important than the discoloration on the untreated samples, although the colour of all the samples turned grey (Fig. 9). This information suggests that the treatment with tannin-based formulations can have a positive effect on colour changes, particularly on brightness (*L** values). This effect will be prolonged as soon as a more elastic anchorage of tannin polymer to wood can be reached.


**Fig. 9.** Visible impression of cracks and changes in colour for untreated (left) and two different tannin-impregnated (10% treated in the middle and 20% treated on the right) samples weathered after 158 days under natural conditions

It is also important to note that after the natural weathering cycle, significant crack formations were observed. In this case, the number and the dimensions of the cracks were more significant for the tannin-treated specimens. In the following table, the trend of the cracks is described (Table 2).

**Table 2.** Description of the Crack Formation During the Natural Weathering Exposure Cycle

| Treatment | Day 1 | Day 44 | Day 88 | Day 123 | Day 158 |
|---|---|---|---|---|---|
| Untreated | Intact | 1 to 3 | 4 to 6 | 4 to 6 | 4 to 6* |
| 10% tannin-treated | Intact | 4 to 6 | 4 to 6 | 7 to 10 | 7 to 10* |
| 20% tannin-treated | Intact | 4 to 6 | 7 to 10 | 7 to 10* | 7 to 10* |

*= At least one of the cracks completely cross the 15 cm of tangential face

It has to be noted that the timber specimens were always oriented with the tangential face exposed to the degradation agents. This exposure was selected because it is highly susceptible to cracks and significant results were achieved also with shorter exposure (Sandberg 1999).

Even if the single properties such as leaching resistance and biological efficacy are satisfactory, the most significant stress for tannin-based wood preservatives is the outdoor exposure. In these tests, the continuous stress due to dimensional movement and to UV-rays shows the sensibility of these wood preservatives to external exposure.

## CONCLUSIONS

Tannin-hexamine formulations have very interesting properties as wood preservatives. The analysis of the leaching and biological resistance has shown satisfactory results:

1. Resistance to leaching: More than 65% of the preservative resists the very severe leaching conditions of EN 84, while a maximum of 20% of the uptaken preservative is lost after a complete ENV 1250-2 cycle.
2. Biological resistance: Good resistance against *Hylotrupes bajulus* was observed especially when non-invasive leaching methods were applied.

On the other hand, the dimensional stability and the degradation due to weathering provided results that contradict the trend.

1. The dimensional stability, indeed, shows that the treated samples are more sensitive to changing moisture conditions and experience stronger internal stresses. The continuous change in moisture and temperature that occurs during the weathering tests stresses the polymeric structure and forces the rigid tannin-hexamine network to break. The tannin-impregnated samples crack more often and with deeper cracks than the untreated specimens because of a higher swelling coefficient.
2. The artificial and natural weathering provided comparable results in terms of changes in surface colour. The total colour difference $\Delta E^*$ showed that colour of the tannin-impregnated samples has more stability against discolorations than the untreated ones even if the weathered samples tend to turn grey.

The rigidity of the polymer is the key to understanding the process. The combined effect of wood movement and UV-ray exposure stresses the polymer and some branches of the polymer network break, producing lower molecular weight fragments that can be easily leached out. The synthesis of a more elastic polymer will be indispensable for the future of this semi-natural wood preservative. Two types of approaches can be considered in modifying the structure of the polymer:

- Blend with long-chain compounds (*e.g.* PVAc, PEG, fatty acids, and oils)
- Covalent branches with long chain copolymers (*e.g.* ε-caprolactame and long-chain isocyanates)

These two opportunities will be investigated in the near future.

## ACKNOWLEDGMENTS

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