COPPER COMPLEXES GRAFTED TO AMINO-FUNCTIONALIZED SILICA GEL AS WOOD PRESERVATIVES AGAINST FUNGAL DECAY: MINI-BLOCKS AND STANDARD TEST

Sabrina Palanti, a Elisabetta Feci, a Giovanni Predieri, b and Vignali Francesca b

Previous preliminary studies showed good efficacy of treatments based on a mixture of siloxane materials, functionalized with amino groups and coupled with copper, against the brown rot fungus Coniophora puteana (Palanti et al. 2011). In the present work, a one-step impregnation was performed on two sets of samples differing in size, in order to verify and compare the homogeneity of treatments. Leaching and resistance against brown rot and white rot fungi were also tested according to European standards EN 84 and EN 113, respectively. Furthermore, an accelerated test of efficacy against fungal decay was also used for determining the treatment efficacy. The obtained results made it possible to validate the findings of the preliminary study concerning resistance of the treated wood against C. puteana, while extending them to the white rot fungus Trametes versicolor. In contrast, no protection was conferred by the treatment against the copper-tolerant fungus Poria placenta.

Keywords: Alkoxysilane; Sol-gel materials; Coniophora puteana; Trametes versicolor; Poria placenta; Wood modification

Contact information: a: CNR – IVALSA Istituto per la Valorizzazione del Legno e delle Specie Arboree Via Madonna del Piano 10 I – 50019 Sesto Fiorentino (FI) palanti@ivalsa.cnr.it
b: Dipartimento di Chimica G.I.A.F., Università di Parma Parco Area delle Scienze I - 43100 Parma

INTRODUCTION

Conventional wood protection by chemicals is based on a broad array of biocidal formulations, such as copper/organic biocides, copper-organometallics, and metal-free preservatives (Hughes 2004), especially for use class 3 according to EN 335-1 (2006). Several alkyl-ammonium compounds, such as tertiary amine salts and quaternary ammonium compounds are also conventionally utilized as wood preservatives (Pernak et al. 2004).

Alternative methods which allow for improved wood durability without the use of biocides are based on wood modification techniques; in the last 10 years they have developed very fast. One approach followed for modifying wood is to impregnate the cell wall with monomers that are then polymerised in situ. Various monomers have been taken into consideration for this purpose and, among them, alkoxysilanes have been studied (Schneider and Brebner 1985; Ogiso and Saka 1994; Rozman et al. 1997).

Polymerisation of the organo alkoxysilanes monomers can be achieved by free-radical polymerisation or via silanol condensation to form siloxane bonds after hydrolysis of the attached alkoxy groups or also via forming chemical linkages between the hydrolysed silanes and cell wall hydroxyl groups (Sèbe and Brook 2001).

Sol-gel prepared using alkoxysilanes systems causes a delay of fungal attack on wood, while after longer exposure heavy decay occurs (Donath et al. 2004).
combination with other biocides such as boric acid and boron compounds, alkoxysilanes have been shown to confer resistance against fungal decay, larvae of *Hylotrupes bajulus* (Reinsch *et al.* 2002; Terziev *et al.* 2009), and termites (Feci *et al.* 2009).

Hill *et al.* (2004) reported that the organo-alkoxysilanes γ-[methacryloxy)propyl] trimethoxy silane and vinyl trimethoxy silane polymerised within the cell wall of *Pinus nigra* caused resistance against fungal decay at high treatments levels. The combination of silane quaternary ammonium compounds to a SiO$_2$ matrix via a sol-gel process enhanced the preservative properties of the treatment against fungal decay (Donath *et al.* 2006). The antifungal resistance was shown to be due to the amino groups, while alkyl groups influencing the water uptake of wood only had a minor impact. Ghosh *et al.* (2008) and Weigenand *et al.* (2008) showed that amino-silicone emulsions imparted a long-term decay resistance, although the reason for this (either long-term hydrophobization or toxicity) has not been investigated.

Despite all these attempts to protect wood without the use of biocides and despite also the fact that the use of chromate copper arsenate (CCA) has been banned for uses in potential contact with humans (European Commission 1998, Environmental Protection Agency 2002), copper remains the primary biocide component used today to protect wood used in ground contact or fully exposed to weather (Lebow *et al.* 2004).

The characteristics of the alkoxysilanes, exhibiting good fixation into wood and having the possibility to be functionalized with amino groups, can be combined with the biocidal activity of copper, in order to obtain a preservative that combines two different approaches to wood protection: a chemical modification based on silica xerogel and the biocidal action of copper.

In a previous study, Palanti *et al.* (2011) showed the possibility to graft copper Cu(II) into a xerogel matrix derived by the condensation of two alkoxysilanes used as precursors, specifically tetraethoxysilane (TEOS) and 3-aminopropiltriethoxysilane (APTES). Copper cations were thought to be fixed by coordinative interactions with amino groups. Between the two treatments compared in this preliminary study, the one-step one (alkoxysilanes and copper chloride mixed together) exhibited a good efficacy against the brown rot fungus *Coniophora puteana* even after leaching. A 3% level of copper leached out was estimated. Evidence for the penetration of the condensed xerogel into the wood and for the spreading of copper inside the wood by complexation with the amine functions was then provided by Vignali *et al.* (2011) through solid state 29Si NMR, ESR, and SEM/EDX investigations. In Palanti *et al.* (2010), different ratios among ingredients with and without the leaching procedure were tested against the same fungus. A good protection after leaching was conferred by the treatment where TEOS and APTES were in 1:1 volume ratio. No mass loss was found also for the combination without copper.

These findings were obtained by using small size samples, with a low number of replicates and they concerned only one fungus.

Mini blocks for testing the efficacy of new preservatives based on silicon compounds have been used extensively (De Vetter *et al.* 2009, Donath *et al.* 2004, Ghosh *et al.* 2008, Weigenand *et al.* 2008). Although some of the tests were over-extended, the conclusions drawn on the protective effectiveness of the tested treatment should be validated by trials conducted with more conventional procedures, in order to make results comparable with others.
Therefore, in the present work, further investigations were conducted on the formulation based on TEOS-APTES-Cu combinations at the most convenient ratio, impregnated through a one-step treatment, with the following aims:

1. To test the formulation for leaching and decay resistance according to standard procedures (EN 84 1997 and EN 113 1996) and to estimate the copper leaching from standard wood blocks.
2. To test the effectiveness against both brown rot and white rot decay fungi.
3. The objective of this paper was to evaluate a new preservative and to investigate the existing and generally accepted methodologies to determine the efficacy of new products. To achieve this last objective, it was necessary to compare the performance of the impregnation process and the preservative efficacy of the treatment against fungal decay between two groups of samples having differing dimensions.

EXPERIMENTAL

Formulation

The formulation was made of TEOS:APTES, 1:1 in volume ratio and CuCl₂ in molar ratio APTES:CuCl₂ of 1:5. Ingredients were diluted with an equivalent volume of ethanol. A total volume of 1200 mL was prepared (Table 1). The mixture containing TEOS, APTES, ethanol, and CuCl₂ was stirred in a beaker until complete solubilisation of copper salt.

<table>
<thead>
<tr>
<th>TEOS</th>
<th>APTES</th>
<th>CuCl₂</th>
<th>Ethanol</th>
<th>Total solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>mL</td>
<td>mL</td>
<td>g</td>
<td>mL</td>
<td>mL</td>
</tr>
<tr>
<td>300</td>
<td>1344</td>
<td>34.41</td>
<td>250</td>
<td>1200</td>
</tr>
</tbody>
</table>

Wood Samples

Wood blocks of *Pinus sylvestris* L. sapwood were selected; dimensions of mini-blocks and standard blocks were respectively 30 x 10 x 5 mm³ and 15 x 25 x 50 mm³. The number of mini and standard wood blocks was respectively 29 and 28. Before being subjected to the impregnation processes, wood samples were oven-dried at 103 °C, weighed, and re-conditioned to constant mass at 20 °C and 65% relative humidity (RH).

Impregnation

The impregnation process was performed in accordance with EN 113. An impregnation chamber (vacuum - atmospheric pressure) with a 6 L total capacity was used. The mix was stirred before impregnation. Samples were placed into the chamber, covered with a net, and ballasted to avoid floating. Air was pumped out for 15 minutes at 0.7 kPa. Subsequently, the treating solution was allowed to flow in the chamber. After liquid addition, the chamber was slowly brought to atmospheric pressure again. The wood samples were left soaking in the solution for two hours, then after a gentle wipe, they were weighed and placed in the conditioning room. After conditioning, the samples
were oven-dried for 18 h at 103 °C and weighed again. The exposure to oven heating made it possible to finish the reticulation of polymers very fast.

The impregnation process was characterized through the determination of Weight Percent Gain (WPG₁) referred to the anhydrous mass of untreated wood (Donath et al. 2004),

\[
WPG₁(\%) = \frac{M_t - M_0}{M_0} \times 100
\]

where \( M_0 \) and \( M_t \) are the oven-dry weights of untreated and sol-gel treated wood, respectively.

**Leaching**

Wood specimens were subjected to the leaching procedure according to EN 84 (1997). Wood specimens were placed in a glass beaker filled with deionized water conforming to EN ISO 3696 (1996). Wood specimens were prevented from floating by the use of weights. The beaker was put in a desiccator, and vacuum was applied, corresponding to a residual pressure of 4 kPa. Vacuum was maintained for 20 minutes and then released to return to normal pressure. Wood specimens were maintained in water (ratio of water to wood 5:1) for 14 days with 9 water changes, and then conditioned to constant mass.

After leaching and conditioning, samples were dehydrated again as previously described and weighed. The weight percent gain after leaching (WPG₂) was calculated as follows,

\[
WPG₂(\%) = \frac{M_l - M_0}{M_0} \times 100
\]

where \( M_0 \) and \( M_l \) are the oven dry masses of untreated wood and sol-gel treated and leached wood, respectively. The leached formulation (LF) was determined with the following formula, where \( M_0, M_t, \) and \( M_l \) have the same meaning as previously explained:

\[
LF(\%) = \frac{M_t - M_l}{M_t - M_0} \times 100
\]

This formula is equivalent to that used by Panov and Terziev (2009). The correlation coefficient (Pearson R) between initial dry masses and dry masses after treatment and after leaching of both sample groups was calculated in order to verify the uniformity of treatment and to highlight a possible effect of sample dimensions on results. F-test and Wilcoxon rank sum test were used to compare WPG and LF obtained by the two groups of samples.

**Determination of Copper**

Two pairs of specimens with standard dimensions (EN 113, 1996) representative of the treated and the leached groups respectively, were ground and consequently submitted to mineralization with 70% HNO₃ and 40% HF acid in a microwave-oven for
45 minutes at 180 °C. Determination of copper was performed by inductively coupled plasma optical emission spectrometry (ICP-OES), with yttrium as the internal standard. Its content was expressed in mg/Kg of dry matter.

Copper content was also computed as an absolute value (mg) and as a percentage of the dry mass of the formulation impregnating the wood before and after leaching.

**Efficacy Test Against Fungi**

Both treated and untreated control specimens were γ-sterilised before fungal exposure. The European Standard EN 113 (1996) provides for one obligatory fungus, one obligatory fungus for particular hazards, and two supplementary fungi of choice from a list to be used for testing of a wood treatment.

In accordance with these indications, the following biological material was selected: the brown rot fungus *Coniophora puteana* (Schumacher ex Fries) Karsten strain BAM Ebw. 15 (obligatory fungus for softwoods); the white rot fungus *Trametes versicolor* (L.) Lloyd, strain CTB 863 A (obligatory fungus for particular hazards); and the brown rot fungus *Poria placenta* (Fries) Cooke sensu J. Eriksson (FPRL280) (supplementary fungus).

The resistance against rot agents was evaluated through the measurement of the mass loss (ML) of wood, which was calculated for each individual block as the difference between initial dry mass and dry mass after the fungal exposure, corrected by WPG₂:

\[
ML(\%) = \frac{M_0 - M_{0\text{ final}}}{M_0 \times 100 + WPG_2}
\]  

Differently from EN 113, where specific wood specimens (checks) are put in contact with malt-agar medium alone for determining the mass loss not due to fungal decay, the WPG₂ was used as the correction factor, because it represented the gain mass due to treatment after the leaching procedure.

**Mini-block test**

The accelerated methodology proposed by Bravery (1978) was followed, with some modifications due to the arrangement of samples and to the use of Kolle flasks in place of Petri dishes. For each fungus, two groups of four treated samples were placed in two Kolle flasks together with two untreated reference samples of sapwood of *Pinus sylvestris* L. each. In each container, fungal strains were previously grown on 80 mL of 4% malt and 2.5 % agar medium. The wood blocks were incubated with the fungus for eight weeks at 22 °C and 75% RH.

**Standard test**

The standard test was in accordance with EN 113 (1996). One treated sample and one reference untreated sample were placed in one Kolle flask where the fungus was previously grown on the same 4 to 2.5 % malt-agar medium. Eight repetitions for each fungus were used.

Virulence of fungal strains was checked through the exposure of non-treated reference control samples, both in the mini block and the standard test (6 samples).
RESULTS AND DISCUSSION

Treatments

The results obtained respectively with standard and mini wood blocks are described in Table 2. Impregnations were uniform, and in fact dry masses after impregnation had a very low variability. There was a very good correlation between dry masses before and after treatment of both small and standard specimens \((R_{\text{standard}} = 0.91; R_{\text{mini}} = 0.98)\). WPG\(_1\) values for small and standard groups were very different, as well as their variances \((F_{28.27} = 6.550; p = 0.000)\). The small samples gained the most after treatment; their dimensions might allow the treatment to penetrate deeply and completely into wood, while those of standards might not. However, there was a higher dispersion in the WPG\(_1\) values of the small samples, as evidenced by their variance \((\text{mini blocks: } 8.9; \text{standard samples: } 1.4)\)

<p>| Table 2. Results from Impregnation Process of Both Standard and Miniaturized Wood Blocks |
|---------------------------------|----------------|----------------|----------------|</p>
<table>
<thead>
<tr>
<th></th>
<th>(N)</th>
<th>(M_0) g</th>
<th>(M_t) g</th>
<th>WPG(_1) %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean (sd)</td>
<td>Mean (sd)</td>
<td>Mean (sd)</td>
<td></td>
</tr>
<tr>
<td>Mini blocks</td>
<td>29</td>
<td>0.64 (0.08)</td>
<td>0.77 (0.10)</td>
<td>20.1 (3.0)</td>
</tr>
<tr>
<td>Standard</td>
<td>28</td>
<td>8.45 (0.21)</td>
<td>9.42 (0.23)</td>
<td>11.5 (1.2)</td>
</tr>
</tbody>
</table>

\(M_0\) means initial dry mass, \(M_t\) is the oven dry mass after treatment, and WPG\(_1\) is the weight percent gain after treatment. sd = standard deviation

Leaching

Results for leaching are reported in Table 3. Although WPG\(_2\) obtained by standard and mini blocks groups were very different, percentages of leached formulation were very similar, respectively 24.9% and 24.1% and did not differ significantly (Wilcoxon rank sum test: \(W = 415, p\)-value = 0.254; df = 51). Dry masses after leaching of mini and standard samples were highly correlated with dry masses after treatment \((R \text{ value } 0.99 \text{ in both groups})\), as well as with dry masses before treatment \((R_{\text{standard}} = 0.93; R_{\text{mini}} = 0.99)\).

| Table 3. Results from Leaching Test of Standard and Mini Wood Blocks |
|-------------------------------------------------|----------------|----------------|----------------|
|                                                | \(N\) | \(M_0\) g | \(M_l\) g | WPG\(_2\) % | Leached formulation% |
|                                                | Mean (sd) | Mean (sd) | Mean (sd) | Mean (sd) | Mean (sd) |
| Mini blocks                                   | 27   | 0.65 (0.09) | 0.75 (0.10) | 15.3 (2.6) | 24.1 (2.1) |
| Standards                                     | 26   | 8.45 (0.21) | 9.17 (0.22) | 8.7 (1.0)  | 24.9 (1.3) |

\(M_0\) = anhydrous mass after treatment; \(M_l\) = anhydrous mass after leaching; WPG\(_2\) = weight percent gain after leaching. sd= standard deviation. Two impregnated samples for each group were retained for copper determination, therefore they did not undergo leaching.
Determination of Copper

Copper was effectively drawn into the wood, as confirmed by the ICP analyses (Table 4), from which the values of 2446 and 2064 mg/kg on the two impregnated samples were obtained. These values represent respectively 2.3 and 2.0% of the anhydrous formulation uptake. In terms of retentions, the copper fixed into wood was around 1 kg/m³.

Concerning the leached samples (number 3 and 4 in Table 4), the ICP detected a slightly lower copper concentration in the analysed samples: 2021 and 2046 mg/kg respectively, corresponding to a copper retention around 1 kg/m³. Also, in this case, the amount of copper found was about 2.2% of the dry mass of the retained solution after leaching.

It is noteworthy that the copper was present in the formulation in a similar percentage before and after leaching, which was around 2%. This means that copper was tightly fixed into the network formed via the sol-gel process by alkoxysilanes, and the part that was not fixed was leached out together with the other components. The percentage of copper leached out was therefore very similar to the leached formulation, that is around 24%. Vignali (2011) recorded a higher amount of released copper in the first days of leaching in a study with a similar formulation but with different ratios among ingredients. While in the previous study of Palanti et al. (2011), the copper retention was around 4 Kg/m³, in the present study the retention obtained, before and after leaching, was almost 4 times lower. In both cases, the copper leaching is negligible. The difference between the two studies was in the wood block size, that was small (15 x 25 x 30 mm) in the study of Palanti et al. (2011) and standard in the present one (15 x 25 x 50 mm). Different retention values according to sample dimensions also confirm the existence of a sample size-effect on the impregnation process, which has to be taken into account when testing a new preservative. Probably the smaller samples were completely impregnated. In the case of specimens of standard dimensions, the formulation is prevented from going deeply by the size of the alkoxysilane particles and by the sol-gel process that starts taking place at the wood surface.

<table>
<thead>
<tr>
<th>Wood sample</th>
<th>Condition</th>
<th>Dry uptake</th>
<th>Leached formulation</th>
<th>Cu mg/Kg (from ICP)</th>
<th>Cu content1</th>
<th>Cu content in the formulation</th>
<th>Cu retention2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Non-leached</td>
<td>0.988</td>
<td>-</td>
<td>2446</td>
<td>23.0</td>
<td>2.3</td>
<td>1.22</td>
</tr>
<tr>
<td>2</td>
<td>Non-leached</td>
<td>0.981</td>
<td>-</td>
<td>2064</td>
<td>20.0</td>
<td>2.0</td>
<td>1.06</td>
</tr>
<tr>
<td>3</td>
<td>Leached</td>
<td>0.888</td>
<td>22.9</td>
<td>2021</td>
<td>19.0</td>
<td>2.1</td>
<td>1.02</td>
</tr>
<tr>
<td>4</td>
<td>Leached</td>
<td>0.836</td>
<td>24.2</td>
<td>2046</td>
<td>19.2</td>
<td>2.3</td>
<td>1.01</td>
</tr>
</tbody>
</table>

*Notes: 1 derived from the dry mass of the sample (omitted in the table) 2 referred to the green volume of the sample (omitted in the table)

Efficacy Test Against Fungi

The results of the efficacy test with different size wood blocks are reported in Table 5. All fungal strains showed a high virulence. Nevertheless in the mini-block test, some control specimens were not attacked by T. versicolor and P. placenta; therefore, the corresponding treated samples were excluded. Mean moisture content of treated samples
resulted also in a favorable range for fungal development, for both types of test and different fungi. The accelerated test showed a good resistance of treated samples to *C. puteana* and *T. versicolor*, while in contact with *P. placenta*, only four mass loss values, ranging from 0 to 44%, were obtained. Negative values of mass losses after fungal exposure, as those obtained with *C. puteana*, might be explained from a chemical point of view. Hydrolyzed water, gathered from the fungus on the surface of the wood sample, was probably introduced in the siloxanes matrix: the Si–O–Si bonds reacted with H$_2$O, giving rise to two Si–OH groups in the network. The embodied water caused a mass increase in the formulation uptake.

<table>
<thead>
<tr>
<th>Fungus</th>
<th>Treated ML % (m (sd))</th>
<th>Treated MC % (m (sd))</th>
<th>Control ML % (m (sd))</th>
<th>Control MC % (m (sd))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MINI TEST – 8 weeks</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>C. puteana</em></td>
<td>8 -2.6 (2.0)</td>
<td>46.6 (3.6)</td>
<td>4 36.2 (13.9)</td>
<td>46.6 (3.8)</td>
</tr>
<tr>
<td><em>P. placenta</em></td>
<td>4 18.9 (23.1)</td>
<td>43.1 (7.4)</td>
<td>2 58.0 (1.4)</td>
<td>49.9 (0.4)</td>
</tr>
<tr>
<td><em>T. versicolor</em></td>
<td>4 -1.2 (0.2)</td>
<td>33.3 (3.3)</td>
<td>2 21.0 (3.4)</td>
<td>51.1 (0.1)</td>
</tr>
<tr>
<td><strong>STANDARD TEST – 16 weeks</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>C. puteana</em></td>
<td>8 3.4 (3.7)</td>
<td>42.9 (5.0)</td>
<td>8 62.3 (1.7)</td>
<td>49.3 (1.9)</td>
</tr>
<tr>
<td><em>P. placenta</em></td>
<td>8 42.0 (9.6)</td>
<td>40.2 (2.2)</td>
<td>8 62.8 (3.2)</td>
<td>43.5 (3.4)</td>
</tr>
<tr>
<td><em>T. versicolor</em></td>
<td>8 0.0 (0.1)</td>
<td>26.0 (0.8)</td>
<td>8 23.7 (2.5)</td>
<td>45.7 (4.6)</td>
</tr>
<tr>
<td><strong>VIRULENCE – 16 weeks</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>C. puteana</em></td>
<td>6 47.2 (2.3)</td>
<td>45.3 (0.9)</td>
<td>6 50.3 (6.1)</td>
<td>47.1 (2.9)</td>
</tr>
<tr>
<td><em>P. placenta</em></td>
<td>6 22.1 (1.9)</td>
<td>37.8 (2.5)</td>
<td>6 22.1 (1.9)</td>
<td>37.8 (2.5)</td>
</tr>
</tbody>
</table>

ML%: mass loss percentage; MC%: moisture content; m: mean; sd: standard deviation

The EN 113 test gave more reliable results, especially with the brown rot fungus *P. placenta*, against which the treatment was not effective. Specimens were in fact degraded, consuming up to 52% of their dry mass. In the literature, there is evidence that *P. placenta* is copper tolerant (Sierra-Alvarez 2007), and that copper is not locked into the sol-gel-wood interface, but it is still bioavailable after leaching to disturb the action of copper-sensitive fungi. Oxalic acid produced by brown-rot fungi has been proposed as one mechanism for copper tolerance (Green and Clausen 2003), leading to the formation of insoluble, nontoxic copper-oxalate complexes. Moreover, oxalic acid production increases the acidity of substrate, and copper is considerably less fungi-toxic in an acidic environment than under neutral or even alkaline conditions (Humar et al. 2005). Acidity is also a significant factor in copper depletion in the soil, where increased acidity results in greater leaching of copper-chromium-arsenate (CCA) (Edlund and Nilsson 1999; Wang et al. 1998).

Resistance conferred by the TEOS-APTES-copper sol-gel system against the white rot *T. versicolor* is consistent with the mass loss threshold set by EN 113 (3%). With respect to the mass loss caused by *C. puteana*, its mean value is only slightly higher than 3%. This means that with further tests, especially addressed to leaching reduction, the protection conferred by this treatment can be considered adequate against the copper-sensitive organisms.

A possible concern about the utilization of accelerated tests is that the results could be overestimated. The mass losses were in fact lower than the standard ones,
probably due to the better impregnation of the mini-blocks. The shorter time the mini-blocks were in contact with the fungus might also have an overestimation effect on the efficacy of the treatment. Macchioni et al. (2007) has in fact observed a delay of 2 to 3 weeks in the mass and density loss of thin slices of wood since the beginning of fungal exposure, depending on the wood species and the fungus. This delay might have a major influence on the results of an 8-week test, in contrast to a 16-week test. It is important to remark that the effectiveness results obtained by the accelerated tests might be followed by verification with the standard fungal test.

CONCLUSIONS

1. The results for the effectiveness of the treatment obtained by a standard test on the resistance to the fungus C. puteana validates previous findings (Palanti et al. 2011) and extends the evaluations of efficacy to supplementary fungi such as T. versicolor (white rot) and P. placenta (brown rot).

2. In the leached samples, a copper retention of around 1 kg/m³, corresponding to 2.2% of the dry mass of the retained solution after leaching, was calculated; this percentage did not vary significantly after leaching, as it was found to be around 2%. From these evidences, it can be concluded that copper was tightly fixed into the alkoxy silanes network and under a form still bioavailable against the wood decaying organisms; the part that was not fixed was leached out together with the other components.

3. Unfortunately, this treatment did not confer resistance against a copper-tolerant fungus, P. placenta. This drawback might be overcome by the addition of other co-biocides such as boric acid.

4. An important consideration about the utilization of accelerated tests comes out from this research: the results from accelerated tests could be overestimated. In fact, the mass losses of the mini-blocks were lower than the standard ones. This is likely due to a deeper impregnation. Moreover, data from mini-block tests were affected by a higher dispersion of values. It is important to remark that the effectiveness results obtained by the accelerated tests should be followed by verification with standard fungal tests before the registration of a new wood preservative.

ACKNOWLEDGMENTS

The present research was supported by PAT (Provincia Autonoma Trento) under the SOFIE 2 project. Authors wish to thank Mrs. Anna Maria Torniai of CNR IVALSA for the preparation of fungal decay laboratory tests.
REFERENCES CITED


Environmental Protection Agency (2002). “Notice of receipt of requests to cancel certain chromated copper arsenate (CCA) wood preservative products and amend to terminate certain uses of CCA products,” Federal Register 67(36), 8244-8246.


European Committee for Standardization EN 113 (1996). “Wood preservatives. Test method for determining the protective effectiveness against wood destroying basidiomycetes - Determination of the toxic values.”


Article submitted: July 4, 2012; Peer review Completed: August 18, 2012; Revised article received and accepted: October 1, 2012; Published: October 3, 2012.