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Effectiveness of sol-gel treatments coupled with copper and boron against subterranean termites

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ABSTRACT

Wood modification by sol-gel treatments shows many positive features, like antimicrobial properties. Wood was also successfully modified with alkoxysilanes enhancing its resistance against soil micro-organisms. Silver, copper, zinc compounds, boric acid or organic biocides such as alkylammonium compounds may be added to the sol-gel to enhance its biocidal properties. Nevertheless, if some of these active ingredients and compounds are not fixed into wood by chemical reactions, they can be easily leached out by water. To overcome this limitation, a system based on silica sol-gel material starting from alkoxysilanes has been functionalized with organic groups having copper linking function. Sol-gel was also coupled with boric acid. As preliminary tests against the brown rot agent *Coniophora puteana* (Schumacher ex Fries) gave good results, the sol-gel formulations were also tested for their efficacy against subterranean termites. A no-choice test was set up, in two different time scales. Results show that though the sol-gel treatments act in very different ways, all of them are efficacy against subterranean termites. The total mortality occurred in the longer test suggested that active ingredients may be added in lower quantity.

Keywords: sol-gel, wood modification, *Reticulitermes grassei*, TEOS, APTES, no-choice test

1. INTRODUCTION

Sol-gel application by wood impregnation was studied by Saka *et al.* (1992), through the bound water in the cell wall in order to direct the sol-gel process to the cell wall and to achieve the deposition of silicate therein. Sol-gel prepared using TEOS / ethanol system showed resistance against termites (Mai and Militz 2004), decay fungus *Poria placenta* and larvae of insect *Hylotrupes bajulus* (Reinsch *et al.* 2002). Silica sol-gel coatings show also consolidating and antimicrobial properties (Mahltig *et al.* 2008). Wood was also successfully modified with alkoxysilanes enhancing its resistance against soil micro-organisms (Donath *et al.* 2004).
Inorganic sols may be applied not only in their pure form but may also be modified with a broad range of additives. By choosing suitable additives the properties of wood can be widely modified. For instance, to enhance biocidal properties silver, copper, zinc compounds, boric acid or organic biocides such as alkylammonium compounds may be added (Mahltig *et al*. 2008). Nevertheless, if some of these active ingredients and compounds are not fixed into wood by

chemical reactions, they can be easily leached out by water. This risk may occur even when copper is fixed with ethanolamine group to form the most widely used complex for several emerging wood preservatives (Cao and Kamdem 2004). A reduced copper leaching was measured from the wood impregnated with solutions containing carboxylic acids (Humar *et al.* 2005); probably this effect is due to a new favourable pH condition for the reaction between copper/ethanolamine and wood. Systems based on silica sol-gel materials starting from alkoxysilanes may be functionalized with organic groups having copper linking function. These systems could be able to graft and encapsulate copper species avoiding or minimizing copper ions leaching (Fig. 1)

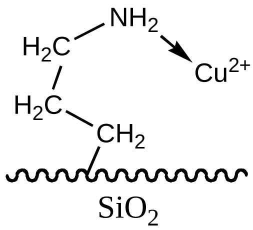

Figure 1: Sketches of the copper grafted to sol-gel

When impregnated into wood, inorganic nanosols condense into a three dimensional xerogel network in which additives may be entrapped. This phenomenon is advantageous to improve the fixation of boric acid, which is another well-known biocidal compound with leaching problems. Boron compounds added to silicon emulsions are already known to be well fixed into wood (Yamaguchi 2003, Nami Kartal *et al.* 2007).
Based on these preliminary remarks, a new sol-gel formulation was created as a wood preservative with a broad spectrum of action, a low environmental impact and a good fixation into the wood. It has been coupled with both copper and boric acid in order to confer the modified wood higher biocidal properties.
While the characterization of impregnation and fixation properties of the new formulation is still in progress, preliminary tests against the brown rot agent *Coniophora puteana* (Schumacher ex Fries) gave good results in terms of mass loss (Palanti *et al.* 2008). The aim of this paper is to test the efficacy of the experimental formulations also against subterranean termites and therefore to define the possible use of the new sol-gel-based preservatives.

2. EXPERIMENTAL METHODS

2.1 Wood sample preparation

Two sets of samples derived from the same board of *Pinus sylvestris* L. sapwood, differing by number and dimensions, were prepared. The samples of series 1 were 1 cm_{rad} x 1 cm_{tang} x 3 cm_{long}, where directions along the grain where indicated by: rad = radial, tang = tangential, long = longitudinal. For each formulation tested seven replicates of series 1 were used. The series 2 was composed by samples of 1.5 cm_{rad} x 2.5 cm_{tang} x 5 cm_{long} and for each formulation a set of four replicates was used. A set of untreated samples used as reference controls was prepared for each series. Before impregnation, samples were oven dried at (103 ± 2)°C, weighed and subsequently conditioned at 20°C and 65% relative humidity until a constant mass was reached.

2.2 Formulations preparation and treatment

Three formulations were selected to test for their efficacy against termites (Table 1). In addition, a silicic acid and a boric acid experimental formulation, whose efficacy against termites is reported in literature (Yamaguchi 2003), was selected for comparison with the previous ones.

2.2.1 Impregnation with silica sol-gel and co-formulates

A solution based on silanes mixture was prepared into a schlenk with the following components: 40.8 ml (0.18 moles) of tetraethoxysilane (TEOS); 7.2 ml (0.03 moles) aminopropyltriethoxysilane (APTES); 12 ml ethanol (EtOH).

The schlenk was linked with a Claisen connector to a glass flask containing 4 small/2 big conditioned wood blocks (Fig. 2). The flask-schlenk system was connected to an oil pump and put under vacuum for 1 hour. By rotation of the system, the solution was poured into the flask with wood samples and maintained under vacuum and hand stirring for 30 minutes and further 30 minutes under nitrogen at 1 atm. After impregnation, samples were conditioned at room temperature and atmospheric pressure. After 1 day conditioning, a set of sample for each series was treated by immersion for two hours in a solution of copper sulphate 0.1 M and a second set of sample per series was treated by immersion for 2 hours with a solution of 0.1 M boric acid. These samples were then dried at room conditions for 24 hours.

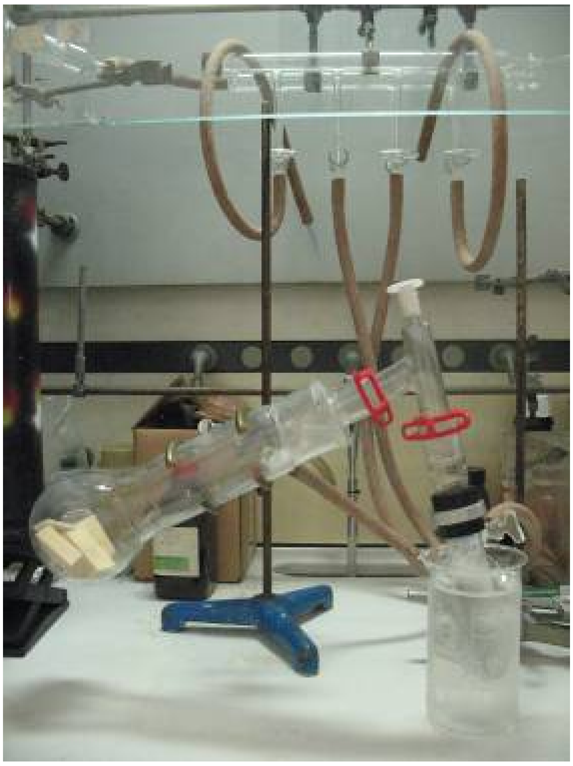

Figure 2: Impregnation system for sol-gel treatments

2.2.2 Impregnation with silicic acid and boric acid

The solution was created by mixing 100 ml of a commercial colloidal SiO_2 (BindzilCC30, Akzo Nobel; SiO_2 30%; pH 9.7; 3.6cP at 20°C) and 4 g of H_3BO_3 diluted in 50 ml H_2O. About 10 l of the solution were prepared for autoclave loading.

Samples were treated by impregnation (Yamaguchi 2005). They were initially placed in a vacuum of 60 mmHg for 30 minutes, and then the pressure was increased by 2 bars every 5 minutes for three times (6 bars). Next, a pressure of 7.7 bars was reached and maintained for 30 minutes. Finally pressure was reduced to normal and the impregnated blocks were dried at 60°C for 48 hours.

For all the formulations of the samples series 1 (Figure 3), the solution uptake was expressed as theoretical weight percentage gain (WPG) (Table 1). Before termites exposure, one treated sample for each series was dried at (103 ± 2)°C so that an initial moisture content was calculated (Eq.1). By attributing the same moisture content to the samples of the respective series, a theoretical impregnated dry mass was derived from each sample (Eq. 2). The difference between theoretical anhydrous mass after treatment and the measured untreated anhydrous mass, expressed as a percentage of the second one, is the theoretical WPG (Eq. 3).

$$Ut = (Mt - Mt_0)/Mt \quad (1)$$

Where:
Ut is the moisture content of the treated sample referred to the initial mass
Mt is the mass treated
Mt_0 is the mass treated after drying

$$ThMt_0 = Mt - Mt * Ut \quad (2)$$

Where:
$ThMt_0$ is theoretical dry mass of impregnated sample

$$ThWPG = (ThMt_0 - M_0)/M_0 * 100 \quad (3)$$

Where:
ThWPG is theoretical weight percentage gain

Table 1: Characteristics of the impregnated samples series 1. TEOS = tetraethoxysilane, APTES = aminopropyltriethoxysilane, EtOH = ethanol. $CuSO_4$ = copper sulphate, H_3BO_3 = boric acid; n= number of replicates

Treatment	**Anhydrous mass (n=7) [g]**		**Theoretical impregnated dry mass [g]**		**Theoretical WPG [%]**	
	mean	*sd*	mean	*sd*	mean	*sd*
1. sol-gel (TEOS - APTES – EtOH)	1.20	0.03	1.51	0.04	25.86	2.94
2. sol-gel + 0.1 M $CuSO_4$	1.18	0.04	1.68	0.08	42.53	3.27
3. sol-gel + 0.1 M H_3BO_3	1.18	0.04	1.49	0.04	26.13	3.78
4. silicic acid - H_3BO_3	1.18	0.02	1.73	0.12	46.95	9.72
5. None (controls)	1.21	0.05	-	-	-	-

Figure 3: Small sample series after impregnation

2.2.3 Exposure to subterranean termites (no-choice test)

To assess the resistance of the modified wood against subterranean termites both the European Standard EN 117 (2005) and an accelerated method as in Nunes (1997) were used. Termites belonging to the species *Reticulitermes grassei* Clément were collected from broken branches and stubs in a mixed forest of *Pinus pinaster* Ait. and *Eucalyptus* spp. situated near Moitas (39º 43’ 85 N; 7º 53’ 08 W, alt. 423 m asl) in Portugal.

In the accelerated test adapted from EN 117, colonies of 150 workers together with 0-3 soldiers and nymphs, depending on the presence in the colony of origin, were established in 200 ml glass jars with moisturised sand (Fontainebleau sand and water, 4:1 v/v) as substrate (Fig. 4). Six replicates per treatment of the small sample series were exposed to the colonies inside the containers and then placed in a climatic room at (24 ± 2)°C and (80 ± 5)% relative humidity for four weeks. The silicic acid - boric acid treated specimens and the untreated ones were also included respectively as reference and virulence controls.

According to the EN 117, four wood samples of series 2 was placed in contact with colonies of 250 workers and some nymph/soldier inside a glass jar on the same substrate of moisturised Fontainebleau sand as previously described. The containers were then maintained at the same climatic conditions as the previous test for 8 weeks.

After exposure, samples were dried at (103 ± 2)°C and by difference with the two dry masses before and after the test the theoretical mass loss (TML) of the tested samples, was calculated.

Test results were expressed in terms of grade of attack, according to the visual scale in EN 117 and mean percentage of survival.

The test is considered valid when at least 50% of the colony survived on the virulence control samples.

To search for significant differences among the results with the treatments, a statistical analysis was done. Since the data did not showed a normal residues distribution neither homogeneity of variances, it was necessary to perform a non-parametric analysis. The results were submitted to a Kruskal-Wallis analysis, for comparing multiple independent samples (different treatments) with the level of significance of 5%. All the statistics were performed with STATISTICA 7.0©.

Figure 4: The *Reticulitermes grassei* no-choice test as adapted from the EN 117 (Nunes 1997)

3. RESULTS AND DISCUSSION

The test was considered valid because the survival of workers in the controls is highly over 50% (average value in the accelerated and the EN 117 tests: 84.6% and 79.1%). Results reported in Table 2 show a different behaviour of termites on the copper and boron sol-gel treatments. The survival of termites on the sol-gel and copper treated wood is better: they do not avoid it (Fig. 5) but they eventually die of hunger since a low TML and grade of attack were registered (Fig. 6). This non-feeding behaviour might explain the complete mortality occurred in the standard test, which is 4 weeks longer than the accelerated one.
Conversely, on the sol-gel and boric acid treated wood (Fig. 6) termites feed avidly, thus causing their own rapid death. Samples showed a grade of attack of 4 (strongly attacked, small specimens) and an average mass loss of 3.6%.
The toxic action of boron is also confirmed by the mortality that occurred in the silicic acid and boric acid treatment (Fig. 6), where termites died within the first four weeks and just caused some attempts of attack (average values: 0.7 and 1.2).
Results obtained on the sol-gel treatment alone are different. It seems that this treatment produced a toxic delayed effect: after four weeks of the accelerated test, termites have a high survival percentage (average 68.0%) and strongly attack the wood, but the standard test resulted in the same strong attack but a complete mortality of workers (Fig. 7). This phenomenon could be explained in terms of chronic toxicity and sublethal dose of silicon that only in a longer period can determine the death of the termites.

Non parametric analysis of accelerated tests results with Kruskal-Wallis (H) statistics indicated that the treatments were significantly different for: survival rate ($H=19.7$, $p<0.01$), degree of attack ($H=27.4$, $p<0.01$) and TML ($H=27.3$, $p<0.01$). The three parameters were submitted to a multiple comparisons test, where:

- The untreated samples' survival rate is significantly different ($p<0.05$) from the silicic acid with boric acid and from sol-gel with boric acid treated samples, which showed significantly lower survival rates than untreated samples;

- For degree of attack, the silicic acid with boric acid samples were significantly different ($p<0.05$) from all the other tests, which showed the highest degree of termites attack, except from the sol-gel and copper treated samples;
- For TML, significant differences were detected between sol-gel and silicic acid + H_3BO_3 ($p<0.01$), this last with no registered theoretical mass loss; the untreated samples were significantly different from: silicic acid + H_3BO_3 and sol-gel + $CuSO_4$ (both with $p<0.01$), which had lower TML percentages.

Non parametric analysis of EN 117 results showed significant differences between the different wood treatments for both parameters measured: survival rate (H=18.7, $p<0.01$) and degree of attack (H=16.2.4, $p<0.05$).
The two parameters were submitted to a multiple comparisons test, where:

- The untreated samples' survival rate is significantly different ($p<0.05$) from all the other treatments ($p<0.01$), because only in untreated samples tests survivor termites were registered;
- For degree of attack, the silicic acid + H_3BO_3 samples were significantly different ($p<0.05$) from sol-gel and untreated samples; both these tests registered the highest attack level.

Table 2: Results of the no-choice tests. Av = average, sd = standard deviation

Treatment	**Accelerated**	**test**	**4 weeks**		**EN 117**	**8 weeks**	
	Sample code	**Survival [%]**	**Attack**	**TML [%]**	**Sample code**	**Survival [%]**	**Attack**
Sol-gel	t1	86.7	4	8.5	T1	0.0	4
	t2	81.3	4	8.1	T2	0.0	4
	t3	83.3	4	7.6	T3	0.0	4
	t4	0.0	4	7.3	T4	0.0	4
	t5	76.0	4	9.0	-	-	-
	t7	80.7	4	5.6	-	-	-
	Av (sd)	**68.0 (33.5)**	**4**	**7.7 (1.2)**		**0.0**	**4**
Sol-gel and $CuSO_4$	t8	53.3	2	0.6	T9	0.0	2
	t9	81.3	3	0.8	T10	0.0	2
	t10	0.0	1	0.6	T11	0.0	1
	t11	71.3	0	0.5	T12	0.0	3
	t12	26.0	3	0.7	-	-	-
	t13	0.0	1	0.6	-	-	-
	Av (sd)	**38.6 (0.6)**	**1.7 (1.2)**	**0.6 (0.1)**		**0.0**	**2.0 (0.8)**
Sol-gel and H_3BO_3	t15	0.0	4	2.2	T5	0.0	4
	t16	0.0	4	1.8	T6	0.0	3
	t17	2.0	4	6.3	T7	0.0	3
	t18	0.0	4	4.3	T8	0.0	2
	t19	31.3	4	4.0	-	-	-
	t20	0.0	4	2.9	-	-	-
	Av (sd)	**5.6 (12.6)**	**4**	**3.6 (1.6)**		**0.0**	**3.0 (0.8)**
Silicic acid and H_3BO_3	t22	0.0	0	0	T13	0.0	1
	t23	0.0	0	0	T14	0.0	2
	t24	0.0	1	0	T15	0.0	1
	t25	0.0	1	0	T16	0.0	1
	t26	0.0	1	0	-	-	-
	t27	0.0	1	0	-	-	-
	Av (sd)	**0.0**	**0.7 (0.5)**	**0.0**		**0.0**	**1.2 (0.5)**
Untreated	c1	96.0	4	14.1	C1	78.8	4
	c2	72.0	4	12.6	C2	78.0	4
	c3	88.0	4	6.9	C3	78.0	4
	c4	84.7	4	16.2	C4	81.6	4
	c5	80.7	4	18.7	-	-	-
	c6	86.0	4	11.2	-	-	-
	Av (sd)	**84.6 (8.0)**	**4**	**13.3 (4.1)**		**79.1 (1.7)**	**4**

Figure 5: Termites tunnels on a sol-gel and copper treated sample

Figure 6: Small samples after the no-choice test. Columns from left to right: controls, sol-gel and copper, sol-gel and boric acid, silicic acid and boric acid treatments

Figure 7: Samples treated with sol-gel after the no-choice test. Left: small specimens; right: EN117 samples

4. CONCLUSIONS

Wood modification with the solution of TEOS, APTES and ethanol coupled with both copper and boron resulted effective against subterranean termites, although the mode of action is very different. While sol-gel and copper seems to act more like as a repellent, boron has a real toxic action and termites die after ingestion of the active ingredient. The sol-gel alone seems to act in another way, hypothetically with a delayed effect or with a chronic toxicity produced by a sublethal dose of silicon, whose effects are evident a long time after the ingestion.
The total mortality occurred in the longer test suggested that active ingredients may be added in lower quantity; in this case, a test to determine the toxicity threshold should be necessary. It can be considered that these tests should be repeated after exposure of wood to a leaching test, in order to assess the fixation of all compounds into the wood. However, if the wood preservatives are intended for indoor use, they do not need such a procedure.

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