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THE INTERNATIONAL RESEARCH GROUP ON WOOD PROTECTION

Section 4 **Processes and Properties**

Optimization of the bi-oleothermal treatment process for wood preservation and fireproofing

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ABSTRACT

The bi-oleothermal© process (combination of oil and heat treatment) is a well mastered alternative method for wood protection. However, the fire behavior and resistance to decay of bi-oleothermally treated wood are not good enough to ensure performance which meets the service standards for outdoor applications such as cladding or decking expected by the market. The aim of the present research project has been to improve this performance by optimizing the linseed oil formulations used at the impregnation stage. Different formulations combining linseed oil, fungicides, insecticides and/or fire retardants were tested under laboratory conditions in order to assess the resistance of oil-treated wood to molds, decay fungi, longhorn beetles, subterranean termites and fire. The results showed that the investigated biological organisms exhibit different levels of susceptibility to oil based formulations. Additionally, the collected data suggested that some inhibition processes might occur between the oil and the active ingredients, lowering the biocide effect of the final formulation. Subsequently, chemical analyses were performed in order to identify the active ingredients both in the oil formulations used for the second bath and inside the treated wood. The measured concentrations of active ingredients were then compared to the expected target values to determine the possible fate of the biocides in the oil formulations (degradation, migration into wood, interaction between the different components).

Keywords: bi-oleothermal treatment, fireproofing, wood preservation

1. INTRODUCTION

1.1. The bi-oleothermal© treatment

The bi-oleothermal© process was developed in France by CIRAD and FCBA (Extended European patent CIRAD N°00981456.7-2113, 1998), with the aim of making wood more stable and less sensitive to decay when used outdoors. This three-stage process is described in Fig. 1.

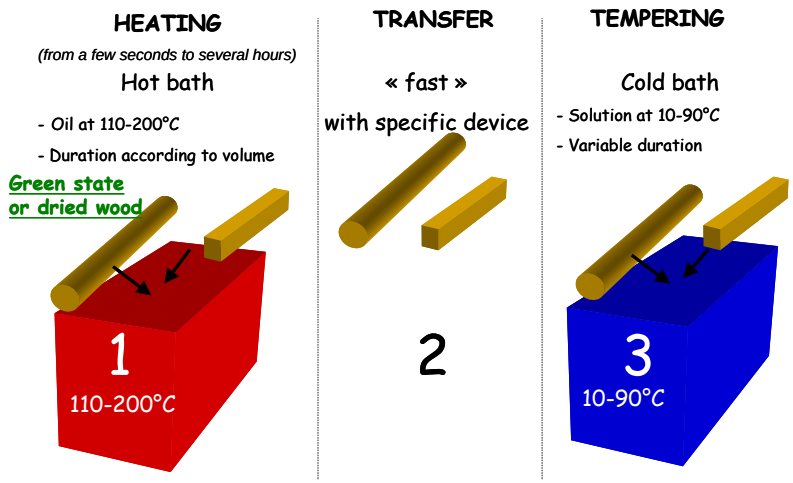


Figure 1: The three stages of the bi-oleothermal© process

The first stage consists in submerging wood pieces in a hot oil bath (between 110°C and 200°C, usually close to 140°C) for the duration necessary to decrease the moisture content of the wood to the targeted level. During the soaking, pressure inside wood cells increases due to the wood's moisture content and high temperature generated in the oil bath. Water in wood lumens progressively vaporizes, first in the outside and then in the central parts of the wood pieces. At the end of this first stage, wood usually contains a significant volume of vapour (the exact amount depending on the duration of the soaking stage and the initial wood moisture content), whose distribution in the wood is not homogeneous. Next, the wood pieces are quickly transferred (stage 2) to the second bath and dipped for a few minutes in cooler oil, whose temperature may range from 10°C to 90°C (stage 3). This stage decreases the temperature of the wood pieces and leads to the condensation of entrapped vapour. A vacuum effect is created inside the wood which allows oil to deeply impregnate it. A description of the thermo-dynamical reactions induced during the process has been extensively done by Grenier (Grenier *et al.* 2007, Grenier 2006,).
The main advantage of this process is achieving deep oil impregnation by operating at atmospheric pressure. The method can also save money as, at least theoretically, it allows the use of green wood. It undergoes fast drying during the first stage, while a full degradation (hydrolysis) of the oil contained in the first bath is induced. Moreover, the process is very simple, requiring inexpensive equipment which is easy to handle.

1.2. Resistance to fungi and insects, resistance to weathering and fire behavior of treated wood: past/earlier research

Different studies were performed in the previous years by the FCBA and CIRAD to evaluate the potential of this type of treatment for wood preservation, resistance to weathering and fire proofing (Podgorski et al, 2007; Podgorski et al, 2008, Simon et al., 2008).
The protective effectiveness of oil treatments against wood destroying Basidiomycetes was earlier tested using five types of oil-based formulations, some being free from biocides and some containing insecticides and fungicides. The tests demonstrated that treatment with biocide-free oils slightly increased the resistance of the treated wood against fungal decay when compared to untreated wood (upgrading the initial natural durability class from 5 to 3-4). Moreover, the maleinization process was shown to significantly improve the performance of oil-treated wood compared to natural linseed oil. Although better durability was obtained by adding biocides, the mass loss measured after exposing wooden samples to fungi was above 3% for all tested treatments, which, according to EN 113 and EN 599 requirements,

indicated that the tested oil treatment was not effective enough to protect wood against Basidicomycete fungi.
The protective effectiveness of oil treatment against termites and longhorn beetles was tested using two oil-based formulations, one with an insecticide and the other without it. Oil treatment alone did not efficiently protect wood as both insects were able to damage it. However, the insects were not able to survive for a long time when oil-treated wood was used as the sole source of food. Wood samples were not attacked by insects and thus regarded as efficiently protected when the insecticide was added to the oil formulation.
Regarding the fire behavior, it was shown that oil treatment had a negative impact on the behavior of wood when exposed to fire, as wood treated with linseed oil did not pass the single-flame source test according to EN ISO 11925-2, leading to a fire hazard classification F (dangerously reactive material), which is the worst possible case. Some other combinations were also tested (traditional fireproofing by phosphate salts impregnation and oil treatment, fire-tested before and after weathering), leading to different fire classification levels, from D to E, after the Single Burning Item test according to the EN 13823 standard.

2. THE PIBOLEO PROJECT

The PIBOLEO project (Multi-functional eco-innovative bi-oleothermal© process of timber preservation and fireproofing) was initiated to allow research centres and industries to work in partnership on oils and eco-additives in order to develop the best solutions for effective protection of wood when used outdoors in above-ground conditions, both against biological organisms and fire threat. In such use conditions, unprotected wood can be damaged by insects (termites and beetles), decay fungi and molds, which are fungi growing on virtually any substance provided moisture is present. Protecting wood against molds is a major challenge in outdoor applications as their development on the surface of coated and uncoated wood also causes aesthetic damage.
As bi-oleothermal© treatment is a well mastered process applicable to many wood species, this research project focused on testing different formulations and the impregnation abilities of various oil-based fluids used during the treatment process. As it was previously established that wood treated with biocide-free oil formulations was not protected effectively enough against fire and biological agents to ensure its good aesthetic and structural durability, we decided to work on oil formulations combining both biocides and fire-proofing agents. However, one of the main challenges is to work with biocide contents which are lower than those used in traditional waterborne wood preservatives. As a single oil treatment is believed to increase the resistance of oil treated wood to wood boring organisms compared to untreated wood, we plan to use biocides only to fill the "durability gap" existing between oil-treated and traditional biocide-treated wood.
The choice of the tested oils and additives (biocides, fire-retardants …) should take into account the targeted end-use for the treated wood products, as the requirements in terms of biological durability and fire regulations can significantly vary depending on the wood's final application (cladding, decking, exterior joinery …). Moreover, all additives need to be as environmentally acceptable as possible.

2.1. The Partnership & the main goal of the project

The PIBOLEO project is based on the following partnership:

- FCBA, CIRAD and LERMAB, which are the main French wood research centres;
- ITERG, a French technical centre for oils;
- Vandeputte Oleochemicals, a Belgian company specializing in the production of linseed oils;
- Oléobois, a French SME specializing in the design and installation of oleothermal wood treatment plants;
- Génération Bois, a French SME which actually uses the industrial prototype of bi-oleothermal wood treatment developed by the CIRAD researchers.

This original partnership was then expanded by adding as technical partners three wood preservation companies: Dyrup SAS, Berkem Développement and Dr Wolman GmbH.

In the bi-oleothermal© process, effective impregnation and thus protection of wood is achieved in the second oil bath. The oil used penetrates the pores of the wood, along with any additives which may be present in the bath. The nature of the second oil bath and of the additives is thus critical since they are responsible for the properties of the final product (wood with the desired characteristics and proper resistance to fire, insects, fungi, UV, etc). The PIBOLEO project is currently focusing on fire-retardant additives and biocides (fungicides, insecticides, etc).

2.2. Focus on the formulation of the second oil bath

The nature of the oil used in the second bath is of paramount importance. The oil should dry as quickly as possible after the impregnation in order to make the wood treatment more convenient for industrial applications. It must also have good oxidative stability in order to allow its use for as many batches as possible. Linseed oils are usually suitable for this application since they contain a lot of unsaturated components (a typical linseed oil contains 50 to 70% of linolenic acid) which facilitate quick drying of the wood. However, these components can also cause the oil's oxidation.

In order to simplify the process, we focused mainly on oil-soluble additives which could potentially be absorbed into the wood together with the oil. The possibility of chemically modifying the oil and grafting additives onto it was also investigated. The oil formulation step was studied independently for fire-proofing and for biological protection as presented in Figure 2.

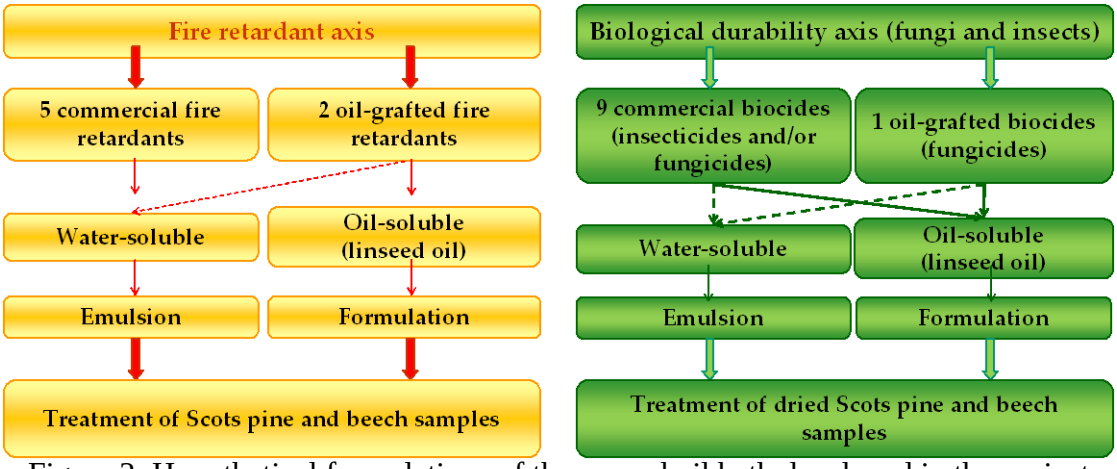


Figure 2: Hypothetical formulations of the second oil bath developed in the project

3. EXPERIMENTAL METHODS

3.1 Wood samples treatment

In a laboratory experiment, samples of Pine sapwood (*Pinus sylvestris)* and Beech (*Fagus sylvatica*) of different sizes were treated using a specially constructed apparatus. A fryer was used for the first oil bath and a jacketed glass reactor coupled with a temperature regulator for the second bath. In the second step, two jacketed glass reactors were used simultaneously, as presented in Figure 3.

Fig. 3: Oil treatment device at the laboratory scale

Depending on the targeted goal (fire-proofing or biological protection), oil-based formulations were obtained by mixing maleinized or linseed oil (Thermoleo® oil, Oléobois) with fire retardants or biocidal active ingredients. The treatment configurations (the size of the treated samples, the duration of the samples' soaking in each oil bath, each bath's temperature) were adjusted to each of the subsequently performed efficacy tests, and are reported in Table 1.
All samples used for the following tests were treated in the same batch and were then sent to the project partners for performance assessment.

Table 1: Oil treatment configurations versus the tests sampling

AXIS	**Tests**	**Sample sizes** (L,R,T) **(mm^3)**	**Oil treatment parameters**	
			1st bath	**2nd bath**
FIRE-PROOFING	Single flame	125x20x88	20 minutes frying in Thermoleo® oil at +120°C	10 minutes soaking at +60°C in tested linseed oil-based formulations
	Cone calorimeter	100x10x100	10 minutes frying in Thermoleo® oil at +120°C	
BIOLOGICAL DURABILITY	Decay fungi	30x10x5	10 minutes frying in Thermoleo® oil at +120°C	
	Molds	50x50x10		
	Subterranean termites	25x25x6		
	Longhorn beetles	50x25x15		

3.2 The fire proofing axis

As many commercial fire retardants are water-soluble, it was first decided to work with oil-water emulsions. However, studying various formulations we identified factors which negatively impacted the effectiveness of the second oil bath (for instance, the emulsion's poor thermal stability and its pollution with components such as wood sap, water and oil originating from the first bath, which limited the possibility of recycling the oil from the second bath). Another concern was to keep the amount of water the emulsion at the minimum to avoid its re-introduction into the wood, which would compromise its durability. Consequently, we decided to stop these investigations (whose results are not presented in this paper) and focus on the grafted oils.

THPC (Tetrakis(hydroxymethyl) phosphonium chloride) is a flame-retardant commonly used in the textile industry (Reeves & Guthrie 1956). It is also well known for easily reacting with oil. That is why THPC was chosen for the study and grafted onto maleinized linseed oil. The grafted linseed oil was assessed for wood fire proofing, as presented in Fig. 4

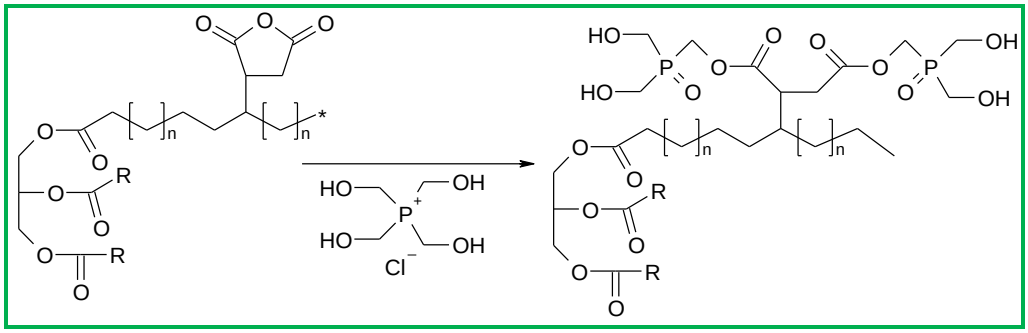


Figure 4: Grafting reaction of THPC on with maleinized linseed oil

An analysis of the newly synthesized products required the development of specific methods based on HPLC (using different columns and different solvent systems), colorimetric assay , ICP and infrared quantitative spectroscopy.

Wood samples treated with different types of grafted oils were subjected to two types of fire tests:

- the single-flame source test according to EN ISO 11925-2. In this test the oil-treated wood samples (Table 2) were exposed to an open a flame for 30 seconds and then observed for another 60 seconds to see if they would ignite and to determine the flame spread distance. Three replicates were used for each tested product. When the tested sample was not inflamed or when the spread of the flame was shorter than 150 mm, Class E, consistent with the EN 130501-1 fire classification standard, was attributed (otherwise it was Class F). The single-flame source test is usually the pre-selection step before running the Single Burning Item test according to the EN 13823 standard.
- when the results of the single-flame source test were not good enough to allow performing the SBI (Single Burning Item) test, the cone calorimeter test was performed according to the ISO 5660-1 standard. The cone calorimeter test measured the heat release rates, the total heat released, and the effective heat induced by the combustion (based on the oxygen consumption principle). The calorimeter also measured the time to ignition when the tested oil-treated wood specimens were exposed to radiant heat fluxes from a conical heater set at 35 and 50 kW/m^2. The samples' dimensions were 75 x 75 mm^2 (that were not the ones required by the ISO standard) and the tests were performed only on three replicates per configuration.

Table 2: Oil-based formulations used for performing the Single Flame tests

2nd bath oil reference	Active substance	% Phosphorus	% linseed oil
M09-0163	**/**	**/**	**100%**
M09-0165	**Grafted THPC onto maleinized linseed oil (70%)**	**0.9 % P**	**30%**

3.3 The biological durability axis

In order to develop oil-based formulations able to efficiently protect wood against biological agents which can potentially damage wood in conditions of use classes 3 and/or 4 (Basidiomycete and Ascomycete fungi, subterranean termites and longhorn beetles – see Figure 5), we selected a total of ten formulations, two of them being biocides-free and eight combining linseed oil with different biocidal active ingredients. Depending on their content, the formulations were tested for known efficiency against fungi and/or insects according to the test methodologies described in the following paragraphs. The studied configurations are presented in Table 3.

Table 3: Oil-based formulations used for performing the biological tests

Code	Composition of the product	Tested organisms				
		Brown rot fungus *C. Puteana*	White rot fungus *C. Versicolor*	Molds	Subterranean termites *Reticulitermes flavipes*	Longhorn beetles *Hylotrupes bajulus*
R/1	**Linseed oil**	**pure**	**pure**	**pure**	**pure**	**pure**
R/2	**Maleinized linseed oil**	**pure**	**pure**	**pure**	**pure**	**pure**
R/3	**Oil + 1 fungicide**	**5 C***	**5 C**	**Not tested**	**Not tested**	**Not tested**
R/5	**Oil + 2 fungicides**	**5 C**	**5 C**	**3+2 C**	**Not tested**	**Not tested**
R/7	**Oil + 4 fungicides + 1 insecticide**	**5 C**	**5 C**	**3+2 C**	**5 C**	**5 C**
R/8	**Oil + 3 fungicides + 1 insecticide**	**5 C**	**5 C**	**Not tested**	**6 C**	**5 C**
R/9	**Oil + 2 fungicides + 1 insecticide**	**5 C**	**5 C**	**Not tested**	**6 C**	**5 C**
R/10	**Oil + 2 fungicides + 1 insecticide**	**5 C**	**5 C**	**Not tested**	**6 C**	**5 C**

*** C = number of tested concentrations**

Figure 5: Experimental set-up for the biological tests performed on oil-treated wood (left to right: Basidiomycetes fungi, subterranean termites, and molds)

All tested concentrations were determined prior to testing in accordance with the specifications of our industrial partners. At least one of the tested concentrations for each product had already proved its efficiency in traditional commercial biocidal formulations.

3.3.1. Fungal decay tests

The fungal tests were performed without any ageing using the test method described by Bravery (1979). Treated wood blocks of Scots Pine sapwood and Beech were exposed to pure cultures of *Coniophora puteana* and *Coriolus versicolor* respectively. Six replicates were used. The fungal strains used are those described in the EN113 standard and were grown on agar-malt media in Petri dishes (9 cm in diameter).

Once sterilized by γ-ray radiation, two treated wood block and one control block were each exposed to fungal attack at 22°C and 70% relative humidity. After six weeks of fungal exposure, the mass loss of each sample was calculated according to the EN113 standard.

The efficacy of two biocide-free oils and six formulations containing fungicide active ingredients was assessed, with six replicates used for each tested concentration. All these products were then tested by, the CIRAD and FCBA.

3.3.2. Mold tests

Three testing methodologies were applied in order to assess mold growth: (1) without ageing, (2) after 6 months of natural weathering, and (3) after 2 weeks of artificial weathering.

First, a laboratory test method was applied which is generally used for determining the minimum concentration of a fungicide, or a formulation of fungicides, that is effective in preventing sapstain fungi and molds development. Scots pine sapwood mini-blocks were treated either by surface application or by deep impregnation in the oil. The mini-blocks were then exposed to *Penicillium funiculosum*, *Aspergillus niger*, and *Trichoderma viride* spore preparations, which were sprayed on the tested samples. Following three weeks of incubation at 22°C, 70% RH, the percentage of the surface covered with molds was visually estimated (according to the guidelines of NF X 41-547). The samples were rated from 0-4, with 4 representing the heaviest mold growth. An inhibition rating of 0 to 1 is indicative of successful mold development inhibition.In order to assess the efficiency of the tested oil-based formulation after weathering, two ageing tests were performed. One set of treated samples was exposed outdoors to natural weathering for six months and then rated as explained above. The other set was first exposed to artificial weathering on an accelerated ageing wheel (where ageing occurs through cycles of samples' high exposure to UV radiation and soaking in cold water) for two weeks, then soaked for one night in cold water, and finally sprayed with spore preparations and incubated for three weeks at 22°C, 70% RH.

The efficacy of two biocide-free oils and two formulations containing fungicide active ingredients was assessed. Three concentrations were chosen to treat the samples by deep impregnation in the oil and two concentrations were used for surface application. Six replicates were used for each tested concentration.

3.3.3. Termite tests

Treated and control Pine sapwood mini-blocks were placed in Petri dishes (9 cm diameter, one wood block per Petri dish). Humid Fontainebleau sand (1 volume of water/4 volumes of sand) was put around the wood block without touching it and one hundred *Reticulitermes flavipes* workers were placed in the sand. The wood samples were exposed for four weeks to termite attack at 27°C, 75% RH. Afterwards, the survival rate of the workers was calculated and the degree of attack was visually estimated (according to the guidelines of the EN117 standard).

The efficacy of two biocide-free oils and four formulations containing insecticide active ingredients was assessed, with six replicates used for each of the six tested concentrations.

3.3.4. Longhorn beetle tests

Treated and control pine sapwood blocks were tested against recently hatched larvae of the house longhorn beetle *Hylotrupes bajulus* according to the guidelines of the EN47 standard. Each block was inoculated with six neonate larvae. After four weeks of exposure, it was determined whether larvae were able to survive and bore through the treated wood.
The efficacy of two biocide-free oils and four formulations containing insecticide active ingredients was assessed, with five replicates used for each of the five tested concentrations.

3.4 Determination of organic biocides concentrations

Follow-up of the biocides concentrations was performed according to FCBA lab methods, currently used for the determination of biocides uptake and specifically made for the Certification controls of treated wood. Measuring biocides concentration inside oil-based formulations or oil-treated wood was made by consecutively weighting aliquots of the product in a glass flask, adding solvents to get the right concentration and dosing the active ingredients by HPLC-DAD spectrometry. UV detection (at different wave lengths specific to each targeted biocide) was then performed for determining the final concentration.

4. RESULTS AND DISCUSSION

4.1 The fire retardant axis

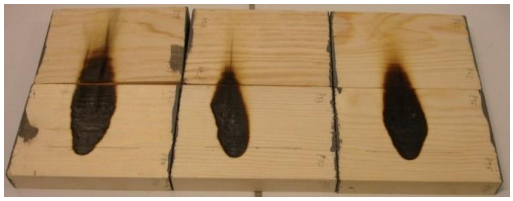
4.1.1. The single flame test according to the EN ISO 11925-2 standard

As already mentioned, only the results obtained with grafted oil are presented. Table 4 presents the fire behavior of untreated Scots pine and of wood samples treated either with blown linseed oil or with grafted (THPC) maleinized linseed oil. The wood samples were end-sealed with epoxy resin prior to treatment in order to limit the oil uptake.

Table 4: Tests results on 3 different configurations

2nd oil bath reference	Samples reference	Average Oil uptake (kg/m3)	Flame extinction (s)	Max flame height (mm)
Untreated Scots Pine	P33+P79	/	90	90
	P79+P33		31	50
	P96+P42		90	95
	P42+P96		90	90
	P59+P40		31	50
	P40+P59		90	120
M09-0163	P31+P74	121.5	32	55
	P74+P31		90	70
	P86+P53		39	60
	P53+P86		31	50
	P83+P52		90	120
	P52+P83		31	50
M09-0165	P111+P102	147.7	32	55
	P102+P111		32	40
	P117+P119		90	110
	P119+P117		32	45
	P118+P110		35	45
	P110+P118		45	50

The residual flame effect is shown for all configurations in the following pictures.



Untreated Scots Pine

Linseed oil treated wood without any additives (M09-0163)

THPC grafted on maleinized oil treated Scots Pine (M09-0165)

Fig. 6 Single-flame source test results according to EN ISO 11925-2

The single flame tests showed that the treated samples displayed better fire behavior than the untreated ones. Despite the fact that deviation is often high in such screening tests, the potential of the grafted maleinized oil with THPC seemed interesting. To better explain these results, phosphorus concentrations were measured in oil-treated wood samples. However, no significant difference was reported between oil grafted with THPC and linseed oil.

4.1.2. The cone calorimeter test according to the ISO 5660-1 standard

THPC-grafted oil was then tested after scaling-up in the cone calorimeter test configuration. Treatment with maleinized linseed oil at two different maleinization rates (HLM 0.5M and HLM 1M) was tested as reference and compared to two maleinized oils with different rates of THPC-grafting (D124 and D125).

Table 5: Cone calorimeter test results with five different treatment configurations

Radiant heat fluxes	Treated wood configuration	Average oil uptake (kg/m^3)	TTI: time to ignition (s)	PHRR : peak for heat release rate (kW/m^2)	AHRE :Average heat release (kW/m^2) 300s	THR (Total Heat Release) (MJ/m^2) 300s
35 kW/m^2	***Untreated wood***	***/***	***45***	***187,3***	***79,4***	***23,8***
	HLM 0,5M	**282.4**	**72**	**351,6**	**179,7**	**53,9**
	HLM 1M	**225.3**	**53**	**346,8**	**157,4**	**47,2**
	D124	**267.7**	**60**	**310,5**	**163,9**	**49,2**
	D125	**182.0**	**36**	**292,2**	**124,3**	**37,3**
50 kW/m^2	***Untreated wood***	***/***	***19***	***205,8***	***118,6***	***35,6***
	HLM 0,5M	**282.4**	**16**	**447,9**	**246,4**	**73,9**
	HLM 1M	**225.3**	**20**	**379,3**	**210,1**	**63,1**
	D124	**267.7**	**17**	**416,5**	**211,3**	**63,4**
	D125	**182.0**	**14**	**382,5**	**157,2**	**47,2**

Experimental curves are reported below for 35 kW/m² radiant heat flux:

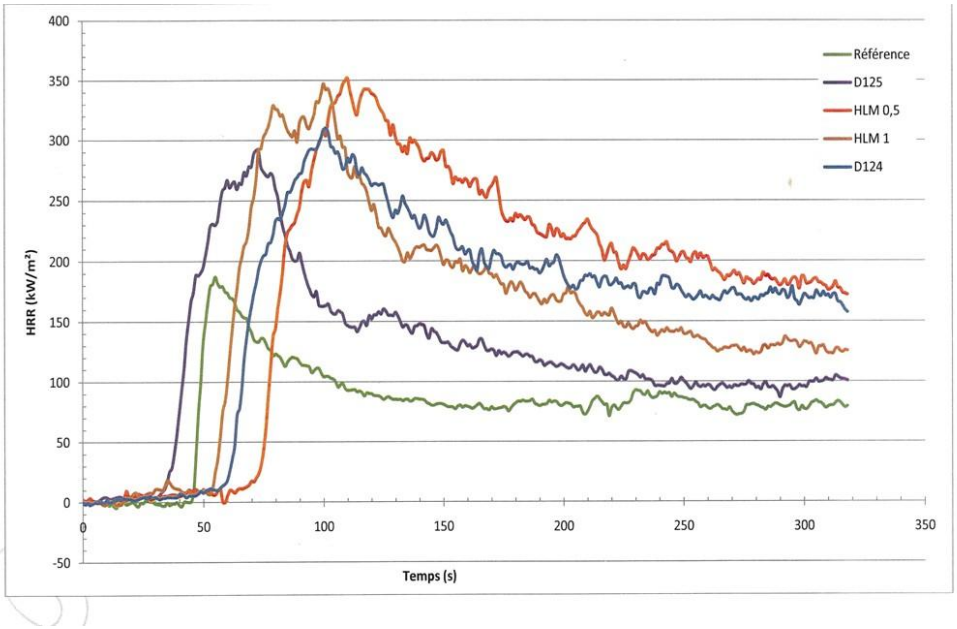


Figure 7: Cone calorimeter test results according to the ISO 5660-1 standard for 35 kW/m² heat flux

The AHRE and PHRR values can be compared between the different configurations and correlated to density and final uptake of the oil formulation used for impregnation in the second bath. The total mass uptake was very similar in several of the tested configurations. However, as the tested oils had different densities (HLM 0.5M < HLM 1M and D124<D125) and different viscosity rates, we may assume that the final oil content of the wood samples might be lower when impregnated with high density and viscosity oils. Time to ignition was shorter in the case denser oils, such as D125, probably because of lower oil content in the treated wood. Time for recovering HRR of reference untreated wood was also shorter, probably because all the oil with which the wood had been impregnated was burnt (after 220 seconds for D125).
The PHRR can be correlated to the oil uptake of the treated wood, but it may also be slightly influenced by the THPC grafting rate (different between D124 and D125). Still, compared to untreated wood, the fire behavior of the tested samples does not satisfy the requirements for ignition and transfer to Single Burning Item test (according to EN 13823 standard) cannot be performed.

4.2. Resistance against wood decaying fungi (brown and white rot)

The results (mean mass loss values) of the fungal tests are given in Table 6.
The control samples displayed usual mass loss values, indicating that fungal damage was in the range of standard requirements. Moreover, all untreated samples placed in the same Petri dish with the treated samples displayed mass loss higher than 20%. The oil was really well fixed and impregnated in the wood and there was no significant exudation of the oil inside the Petri dish (although a very high relative humidity was noticed in each Petri dish). The standard deviation of screening test results for all formulations was very low.
The samples' final full drying was achieved after more than the 24 hours in CIRAD tests, as some samples still displayed detectable moisture content after that time. In FCBA tests, the drying step was completed after 24 hours and no oil exudation was observed.

With oil-treated samples, the decay was significantly decreased from 40% of mass loss (reported for untreated samples) to levels lower than 10% for *C. puteana* on Scots Pine sapwood, and only about 1-2% for *C. versicolor* on Beech.

Table 6: Results of the fungal tests

Product and Concentration		Oil uptake (kg/m^3)		Mass loss (% m/m)			
				C. puteana		*C. versicolor*	
		C. puteana	*C. versicolor*	Treated	Control	Treated	Control
Virulence control				42.91		31.54	
R/1		368.5	315.1	5.5	45.4	2.1	32.2
R/2		375.4	358.2	9.6	48.1	2.5	28.8
R/3	**C1**	364.4	330.3	7.5	47.9	2.2	33.5
	C2	385.7	312.1	7.9	47.5	2.1	26.4
	C3	368.2	333.9	6.4	46.8	1.7	27.5
	C4	366.2	320.6	5.4	40.7	1.9	32.4
	C5	360.7	321.1	4.8	45.0	1.5	30.0
R/5	**C1**	380.0	324.7	6.5	36.5	1.9	27.6
	C2	365.9	326.7	4.9	38.1	2.3	26.5
	C3	390.7	324.0	5.5	36.9	2.6	25.0
	C4	385.7	333.8	6.0	46.1	1.6	27.5
	C5	373.8	329.0	6.5	44.9	2.3	28.5
R/6	**C1**	380.2	310.4	5.3	45.2	2.7	34.8
	C2	379.0	328.7	6.2	46.8	2.2	31.0
	C3	375.8	322.2	7.9	47.1	2.3	30.7
	C4	370.3	332.9	10.4	44.2	2.1	32.5
	C5	371.2	325.4	6.8	45.6	2.0	23.9
R/7	**C1**	372.3	324.8	8.7	43.9	2.2	22.2
	C2	374.2	329.2	7.5	46.7	2.0	31.1
	C3	370.9	328.0	4.7	41.5	1.9	34.1
	C4	382.7	322.5	6.2	41.9	1.3	25.6
	C5	370.8	319.7	6.1	39.8	1.8	29.4
R/8	**C1**	374.2	325.3	7.2	39.5	1.7	31.4
	C2	392.4	325.3	8.1	39.2	2.0	33.7
	C3	352.2	329.1	4.9	35.7	1.7	33.0
	C4	391.0	321.6	3.8	35.1	1.6	29.8
	C5	394.8	347.9	6.6	39.9	1.3	32.3
R/9	**C1**	358.4	323.6	9.6	35.5	1.6	34.9
	C2	357.3	329.6	6.9	37.9	1.7	35.3
	C3	373.1	333.5	5.8	33.0	1.4	32.6
	C4	371.4	308.5	6.1	40.7	1.4	35.7
	C5	373.3	326.1	9.5	41.3	1.7	35.3
R/10	**C1**	364.6	316.6	12.1	45.1	1.3	34.5
	C2	367.7	318.2	6.1	41.8	1.7	31.4
	C3	365.9	337.5	6.6	43.3	1.3	31.1
	C4	360.3	313.2	9.4	43.5	1.5	32.8
	C5	370.3	341.3	4.0	44.6	1.5	36.6

The use of different fungicides, at any concentration, did not affect the final resistance to both wood decay fungi (Figure 8).

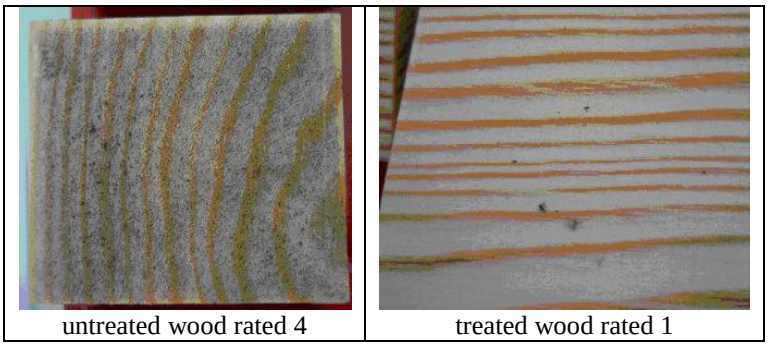
The mass loss reported after exposing treated wood samples to *C. versicolor* was lower than 3%) for all the tested formulations at any concentration, demonstrating that the hydrophobic effect of oil was sufficient to protect wood against this white-rot fungus, or that the time of exposure was not sufficient to allow the fungus to colonize the wood (Unga & Militz 2005). This result is consistent with the known features of *C. versicolor*'s physiology, as this species requires high wood moisture contents for growing. Performing leaching or weathering tests and increasing the time of exposure to fungi should allow us to both confirm the above results and assess the resistance of oil-treated wood against this fungus in real use conditions.

Fig. 8: Exposure of treated wood samples to *C. versicolor* (left)
and *C. puteana* (right)

In contrast, the mass loss after exposing treated wood samples to *C. puteana* was higher than 3% for all the tested concentrations and products, demonstrating that wood was not efficiently protected even when high concentrations of biocidal active ingredients were added to linseed oil. These observations suggested that some inhibition phenomena might occur during the treatment in the second oil bath (limited migration of the active ingredients into wood, thermal degradation, phase separation, interaction with oils…) and then might negatively affect the efficiency of the selected fungicides. As the range of the tested concentrations was, at least theoretically, wide enough to target values which should efficiently protect wood, the possibility of the occurrence of inhibition phenomena has to be considered.

4.3. Mold resistance

Mold development was rated from 0 (no development) to 4 (>50% of the wood surface) (see Figure 9). The results of the tests are presented in Table 7.



untreated wood rated 4 | treated wood rated 1

Fig. 9: Mold development on the wood surface: examples of rating

No mold growth was observed on naturally weathered treated samples, but all of them were affected by blue stain development.
Samples treated by surface application and submitted to wheel ageing displayed also blue stain contamination. All samples treated by deep impregnation, except with R/1 (blown linseed oil), were not affected by fungal development.

Table 7 Results of anti-mold protective efficiency

Product and Concentration (m/m %)		Without weathering			After six months of natural weathering			After two weeks of artificial weathering		
		Impregnation		Surface application (200 g/m²)	Impregnation		Surface application (200 g/m²)	Impregnation		Surface application (200 g/m²)
		Oil uptake (kg/m³)	Mold rating	Mold rating	Oil uptake (kg/m³	Mold rating	Mold rating	Oil uptake (kg/m³	Mold rating	Mold rating
untreated control		/	6/4*	6/4	/	6/0	6/0	/	6/4	6/4
R/1		259.5	6/0*	6/0	188.9	6/0	6/0	319.8	6/0	6/0
R/2		219.6		5/0-1/1	184.1		6/0	256.8		6/0
R/5	**C1**	269.9		6/0	264.2		6/0	252.6		6/0
	C2	234.6		6/0	266.7		6/0	260.8		6/0
	C3	255.1		Not tested	263.4		Not tested	251.9		Not tested
R/7	**C1**	269.6		4/0-2/1	260.7		6/0	287.2		6/0
	C2	265.9		3/0-3/1	265.4		6/0	231.3		6/0
	C3	273.3		Not tested	233.2		Not tested	256.2		Not tested

* 6/4 = 6 samples rated 4

4.4. Resistance against termites

Resistance against termites was tested with different oil formulations. The degree of attack (ranging from 0= no attack to 4= strong attack) and percentage of surviving workers after four weeks of exposure are reported in Table 8.

Table 8: Results of termite tests

Product and Concentration (m/m %)		CIRAD			FCBA		
		Oil uptake (kg/m³)	Termites		Oil uptake (kg/m³)	Termites	
			Degree of attack	Average survival workers (%)		Degree of attack	Average survival of workers (%)
untreated control		/	6/4*	80	/	6/4	65
R/1		321.9	2/1-2/2-2/3**	3	314.1	3/1-3/2	0
R/2		333.1	6/2	0	325.4	3/2-3/3	21
R/7	**C1**	338.3	2/0-1/1-3/2	0	337.7	3/2-3/3	8
	C2	309.7	2/0-2/1-2/2		323.9	6/2	1
	C3	321.7	4/0-1/1-1/2		318.0	2/1-4/2	0
	C4	329.6	3/0-3/1		324.4	4/1-2/2	0
	C5	300.7	3/0-3/1		282.9	3/1-3/2	0
R/8	**C1**	***Not tested***			289.9	2/2-4/3	0
	C2				329.5	2/2-4/3	0
	C3				292.4	5/2-1/3	0
	C4				299.9	6/2	0
	C5				310.2	4/1-2/2	0
	C6				301.8	1/0-5/1	0
R/9	**C1**	257.6	1/2-3/3-2/4	0	304.6	1/1-5/2	0
	C2	287.7	1/1-3/3-2/4		277.2	3/1-3/2	2
	C3	330.2	1/0-4/1-1/2		289.2	6/2	0
	C4	285.7	2/1-4/2		313.1	6/1	0
	C5	310.5	2/0-4/1		308.0	6/1	0
	C6	312.2	3/0-3/1		303.0	4/1-2/2	0
R/10	**C1**	326.0	1/0-1/1-2/2-2/4	0	***Not tested***		
	C2	334.3	2/1-1/2-2/3-1/4	0			
	C3	302.9	3/1-3/2	0			
	C4	305.1	1/0-3/1-2/2	0			
	C5	285.6	1/0-4/1-1/2	0			
	C6	330.7	6/1	0			

* 6/4 = 6 samples rated 4

** 2/1-2/2-2/3 = 2 samples rated 1 – 2 samples rated 2 – 2 samples rated 3

The test can be regarded as valid as the workers survival rate was above 50% and the visual rating of 4 (strong attack) was reported for untreated controls.
In a forced-feeding environment, all the tested formulations, including linseed oil free from biocides (R/1 and R/2), appeared to be toxic for termites, as their mortality was 100% at the end of the test for almost all configurations (except with formulation R/2 in the case of the tests performed by the FCBA).
In the tests performed by the CIRAD, a dose-response effect was reported for all of the formulations containing insecticides (R/7 to R/10), with the three highest tested concentrations inducing significantly lower degrees of attack on the treated samples compared to biocide-free oils (R/1 and R/2). In contrast, in the tests performed by the FCBA, only the highest concentration of the R/8 induced a lower attack of the treated samples.
These results are surprising considering the fact that the biocides used in the oil formulations are well-known, and their efficiency against termites in waterborne or solvent-based formulations has been proved. Thus, we may assume that some uncontrolled and unexpected phenomena occurred during the treatment process, lowering the uptake or the efficacy of the tested active ingredients (possible inhibition reactions with oils, as already suggested on the basis of the fungal decay tests).

4.5. Resistance against longhorn beetles

Resistance against longhorn beetle larvae was tested with different oil formulations. The ability of neonate larvae to damage wood samples and the number of surviving larvae after four weeks of exposure are reported in Table 9.

Table 9: Results of longhorn beetle tests

Product and Concentration (m/m %)		Oil uptake (kg/m^3)	number of larvae that bored into wood	Number of surviving larvae	Product and Concentration (m/m %)		Oil uptake (kg/m^3)	number of larvae that bored into wood	Number of surviving larvae
R/1		266.3	14/18	14/18	**untreated control**		14/18	14/18	14/18*
R/2		226.9	9/18	1/18					
R/7	**C1**	240.7	12/30	0/30	**R/9**	**C1**	302.9	1/30	0/30
	C2	238.6	12/30			**C2**	291.3	0/30	
	C3	257.8	2/30			**C3**	288.0	0/30	
	C4	261.7	3/30			**C4**	314.1	0/30	
	C5	256.1	3/30			**C5**	258.8	0/30	
R/8	**C1**	280.6	0/30	0/30	**R/10**	**C1**	273.8	19/30	1/30
	C2	270.9				**C2**	294.9	1/30	1/30
	C3	180.8				**C3**	280.4	0/30	0/30
	C4	281.5				**C4**	282.2	1/30	1/30
	C5	287.1				**C5**	286.7	0/30	0/30

14/18* 14 larvae survived out of the 18 that were inoculated into the wood

The larvae were able to bore into wood samples treated with blown linseed oil (R/1) and the larval mortality was low (identical to what was reported for untreated wood).
Several larvae were able to bore into wood samples treated with maleinized linseed oil (R/2) but the larval mortality was high, indicating the protective efficiency of the oil itself.
Except at low concentrations of the formulations R/7 and R/10, larvae were not able to bore into wood samples treated with oil formulations containing insecticides. In all cases, close to 100% mortality was reached after four weeks of exposure.
Unlike the termite tests, the longhorn beetle tests demonstrated an effect of the addition of insecticides to oil formulations However, longhorn beetle larvae are usually more sensitive to insecticides than termites, and might thus be affected by much lower concentrations.

4.6. Follow-up of the biocides in treated wood

As a wide range of different biocidal active ingredients concentrations were studied, a tracking of these substances in the treated wood (3 fungicides and 3 insecticides) was performed in order to confirm the uptake of the targeted doses by comparing the measured and theoretical values (designated as M and T in Table 10).

Table 10: Biocidal molecules tracking in treated wood (M) and comparison to the expected values (T) for three different fungicides and insecticides used in five different formulations

Retention of the active ingredients (kg/m^3)	Fungicides				Insecticides			
	Beech		Scots pine		Beech		Scots pine	
	T	M	T	M	T	M	T	M
R/5	1.94	0.30	2.53	0.40				
R/7	12.00	2.58	5.54	0.95				
R/8	12.50	1.84	4.65	0.53	12.50	6.70	4.65	1.65
R/9	25.30	5.35	9.50	1.66	25.30	9.24	9.50	3.28
R/10	26.90	6.30	10.90	2.28	26.90	10.80	10.90	4.30

The results show a huge difference between the targeted values and those measured in the wood samples, for all of the tested fungicides and insecticides.
The values measured for the fungicides were 4 to 6 times smaller than the expected target values for both wood species, which indicates that the active ingredients were either destroyed in the bath or did not penetrate into the wood samples with the oil.
In the case of the insecticides, the measured values were about 3 times smaller than the expected ones.
Such a difference between fungicides and insecticides can be explained by their chemical properties. Fungicides usually display hydrophilic properties and do not easily mix with oils, while insecticides are usually more hydrophobic. Consequently, the penetration of fungicides into the wood during the bi-oleothermal treatment may be lowered due to phase separation with the oil. This effect is significantly smaller in the case of insecticides.
These observations could also explain why a dose-response effect was observed in the termite tests as opposed to the fungal tests.
Additional tests are currently being performed to measure the different concentrations of biocides during the treatment at all stages of the process (in the oil before heating, after the thermal shock due to the introduction of the heated wood samples in the cooler second bath, in the wood after impregnation and in the oil at the end of the process).

5. CONCLUSIONS

Effective fire-proofing of oil-treated wood is of major concern with regard to timber construction legislation. Therefore, this axis is critical for many applications, such as cladding
Test performed for the fire-proofing evaluation showed that maleinized linseed oil grafted with THPC does not protect treated wood when challenged with fire in single-flame and cone calorimeter tests. Moreover, increasing the THPC grafting rates caused many technical problems in developing oil formulations and the treatment process. Future development will focus on the formulation of more stable emulsions integrating surfactants commonly used by the food industry.

Regarding the possibilities of efficient protection of oil-treated wood against biological agents, it appeared that blown and/or maleinized linseed oil itself significantly reduced the

degree of damage induced by most of the tested organisms, which is very encouraging for low-risk above-ground outdoor applications. Oil-based formulations containing biocides (fungicides and/or insecticides) surprisingly did not reach the expected performance levels in terms of wood protection, even when applied concentrations were much higher than those used in traditional wood preservatives. The results suggest that mixing oil and biocidal active ingredients is more difficult than expected, and that some, so far unidentified, interactions or inhibitions may occur, lowering the efficiency of the tested products. Furthermore, the treatment process itself (thermal shock, impregnation of porous materials, and stability of the active ingredients in hot oil …) may impact the final results and needs to be improved.
This preliminary stage of the study allowed us to identify several products which seem promising for scaling-up the process to pilot treatment.

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