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

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THE BI-OLEOTHERMAL TREATMENT

A 3-step wood treatment process developed by FCBA and CIRAD:
1. Dipping in hot oil (120-160°C), leading to the evaporation of the entrapped water and inducing a positive pressure inside of the wood pores
   2. Fast transfer to a second bath
3. Dipping in cold oil (60°C), the thermal shock generating an inversed pressure and inducing the absorption of the fluid (oil + active substances)
THE BI-OLEOTHERMAL TREATMENT

PREVIOUS RESEARCH POINTED OUT SOME WEAKNESSES ...

Biological durability
- Oil treatment only slightly improved the resistance against fungal decay when compared to untreated wood (mass loss >3% with EN 113)
- Termites and longhorn beetles were able to damage wood treated with biocide-free oils

Fire behaviour
- Oil treatment had a negative impact on the fire behaviour of wood = decreased the fire hazard classification to F (dangerously reactive material), which is the worst possible case
- After traditional fireproofing (phosphate salts impregnation), the fire classification levels was increased to D / E

TO BE IMPROVED ...

By incorporating additives: biocides / fire-retardants
**THE CHALLENGE : FOCUS ON THE SECOND BATH TO**

- Improve the fire resistance of the wood by incorporating fire retardants
- Improve the fungi and insect resistance by incorporating optimized amounts of biocides = “fill the durability gap”

### Fire retardant axis

- **5 commercial fire retardants**
- **2 oil-grafted fire retardants**
- **Water-soluble**
- **Oil-soluble (linseed oil)**
- **Emulsion**
- **Formulation**
- **Treatment of Scots pine and beech samples**

### Biological durability axis (fungi and insects)

- **9 commercial biocides (insecticides and/or fungicides)**
- **1 oil-grafted biocides (fungicides)**
- **Water-soluble**
- **Oil-soluble (linseed oil)**
- **Emulsion**
- **Formulation**
- **Treatment of dried Scots pine and beech samples**
## METHODOLOGY

<table>
<thead>
<tr>
<th>Axis</th>
<th>Type of Test</th>
<th>Test Methodology</th>
<th>Sample sizes (L,R,T) (mm³)</th>
<th>Oil treatment parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>FIRE-PROOFING</strong></td>
<td>Single flame</td>
<td>EN ISO 11925-2</td>
<td>125x20x88</td>
<td>20 minutes frying in Thermoleo® oil at +120°C</td>
</tr>
<tr>
<td></td>
<td>Cone calorimeter</td>
<td>ISO 5660-1</td>
<td>100x10x100</td>
<td></td>
</tr>
<tr>
<td><strong>BIOLOGICAL DURABILITY</strong></td>
<td>Decay fungi</td>
<td>Screening test</td>
<td>30x10x5</td>
<td>10 minutes frying in Thermoleo® oil at +120°C</td>
</tr>
<tr>
<td></td>
<td>Molds</td>
<td>NF X 41-547</td>
<td>50x50x10</td>
<td>10 minutes soaking at +60°C in tested linseed oil-based formulations (added or not with biocides and fire-retardants)</td>
</tr>
<tr>
<td></td>
<td>Subterranean termites</td>
<td>EN 117</td>
<td>25x25x6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Longhorn beetles</td>
<td>EN 47</td>
<td>50x25x15</td>
<td></td>
</tr>
</tbody>
</table>
RESULTS OF FIRE RESISTANCE TESTING

The single flame test (EN ISO 11925-2)

<table>
<thead>
<tr>
<th>Samples (6 replicates)</th>
<th>Mean flame extinction (s)</th>
<th>Mean max flame height (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (untreated Scots pine)</td>
<td>70</td>
<td>97</td>
</tr>
<tr>
<td>maleinized linseed oil free from fire-retardants</td>
<td>52</td>
<td>67</td>
</tr>
<tr>
<td>maleinized linseed oil grafted with THPC</td>
<td>44</td>
<td>57</td>
</tr>
</tbody>
</table>

- The treated samples displayed better fire behavior than the untreated ones.
- The potential of the grafted maleinized oil with THPC seemed interesting.
RESULTS OF FIRE RESISTANCE TESTING

The cone calorimeter test (ISO 5660-1)

- HRR: maleinized oil > grafted oil > untreated wood
  - slight improvement with THPC but not enough

- HRR 0.5M > 1M maleinized oil and % > % THPC grafted oil
  - probably because of higher oil uptake (lower viscosity)

Untreated Scots pine
maleinized oil (0.5 M)
maleinized oil (1 M)
THPC grafted oil (%)
THPC grafted oil (%)
RESULTS OF BIOLOGICAL DURABILITY TESTING

Resistance against wood decaying fungi (Bravery screening tests - FCBA/CIRAD)

<table>
<thead>
<tr>
<th>Samples (6 replicates)</th>
<th>Mean mass loss (%)</th>
<th>C. puteana</th>
<th>C. versicolor</th>
</tr>
</thead>
<tbody>
<tr>
<td>control (untreated Scots pine &amp; beech)</td>
<td>&gt; 40</td>
<td>&gt; 30</td>
<td></td>
</tr>
<tr>
<td>biocide-free oils (2 formulations)</td>
<td>&gt;3 (~ 7.5)</td>
<td>&lt; 3</td>
<td></td>
</tr>
<tr>
<td>oils with fungicides (7 formulations/5 concentrations*)</td>
<td>&gt;3 (~ 6.8)</td>
<td>&lt; 3</td>
<td></td>
</tr>
</tbody>
</table>

* Ce/3 < C < Ce*2

- No effect of the added fungicides = inhibition during the process?
- No dose-response (~ same results with all tested products and concentrations)
- Lower fungal growth than controls

- Linseed oil efficiently protect wood against CV?
- Moisture content too low to allow CV growth?
- No additional effect of the tested fungicides

Biocide-free oils improved wood durability (DC 2 in EN350)
### RESULTS OF BIOLOGICAL DURABILITY TESTING

. Mold tests (NF X 41-547 …)

- Mold strains: *P. funiculosum*, *A. niger*, and *T. viride*
- Mold development was rated from 0 (no development) to 4 (>50% of the wood surface)

<table>
<thead>
<tr>
<th>Samples (6 replicates)</th>
<th>Mold rating</th>
<th>Lab test (spore inoculation) without weathering</th>
<th>6 months of natural weathering</th>
<th>2 weeks artificial weathering + spore inoculation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>impregnation</td>
<td>surface application</td>
<td>impregnation</td>
</tr>
<tr>
<td>biocide-free oils (2 formulations)</td>
<td>6/0</td>
<td>11/0 – 1/1</td>
<td></td>
<td>6/0</td>
</tr>
<tr>
<td>oils with fungicides (2 formulations/3 concentrations)</td>
<td>6/0</td>
<td>6/0</td>
<td>3/0 – 3/1</td>
<td>6/0</td>
</tr>
</tbody>
</table>

* 6/4 = 6 samples rated 4

- **Slight mold growth with one tested biocide**
- **No mold growth but 100% blue stain**
- **No mold growth but blue stain with surface application**

Efficient anti-mold protection of the tested oil formulations
Results of biological durability testing

Resistance against the longhorn beetles *H. bajulus* (EN 47)

Ability of neonate larvae to damage wood samples
Number of surviving larvae after 4 weeks exposure

<table>
<thead>
<tr>
<th>Samples (6 replicates)</th>
<th>% of larvae that bored wood</th>
<th>% of surviving larvae</th>
</tr>
</thead>
<tbody>
<tr>
<td>control (untreated Scots pine)</td>
<td>78</td>
<td>78</td>
</tr>
<tr>
<td>biocide-free oils (linseed oil &amp; maleinized oil)</td>
<td>78</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>oils with insecticides (4 formulations / 5 concentrations)</td>
<td>0 (2 F)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0 - 63</td>
<td>0</td>
</tr>
</tbody>
</table>

The larvae were able to bore into wood samples treated with blown linseed oil

Maleinized oil showed a protective efficiency

Except at low concentrations of 2 formulations, larvae were not able to bore into wood samples treated with oil formulations containing insecticides

In all cases, close to 100% mortality was reached

Efficient protection of biocide-free maleinized oil and insecticide added formulations
Resistance against *R. flavipes* termites (EN 117)

The degree of attack after 4 wks exposure ranged from 0= no attack to 4= strong attack

<table>
<thead>
<tr>
<th>Samples (6 replicates)</th>
<th>Degree of attack</th>
<th>Survival %</th>
</tr>
</thead>
<tbody>
<tr>
<td>control (untreated Scots pine)</td>
<td>all rated 4</td>
<td>80</td>
</tr>
<tr>
<td>biocide-free linseed oils (2 formulations)</td>
<td>ratings from 1 to 3</td>
<td>0 - 21</td>
</tr>
<tr>
<td>oils with insecticides (4 formulations/ 5 to 6 concentrations)</td>
<td>ratings from 0 to 3</td>
<td>0</td>
</tr>
</tbody>
</table>

*Except 1P/1C = 8%

**Biocide-free oils do not efficiently protect wood**

**Biocide-free oils are toxic as the mortality was 100% at the end of the test for almost all sets**

A dose-response effect was reported for all formulations containing insecticides with the 3 highest tested concentrations for CIRAD test and only the highest for FCBA test

Biocide-free oils did not avoid termite attacks but are toxic

Tested insecticides showed unexpected bad efficacy, suggesting that their uptake or efficacy have been lowered during the process (inhibition reactions with oils?)
3 fungicides and 3 insecticides were tracked in the treated wood samples to confirm the uptake of the targeted doses by comparing measured and theoretical values (M and T).

| Retention of the active ingredients (kg/m²) | Fungicides | | Insecticides | | |
|---|---|---|---|---|
| | Beech | Scots pine | | Beech | Scots pine |
| 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 |

- Huge difference between the targeted values and those measured in the wood samples, for both species and all of the tested fungicides and insecticides: 4-6 X smaller for fungicides / 2-3 X smaller for insecticides.

The active ingredients were either destroyed in the bath or did not penetrate into the wood samples with the oil.

Subsequent tracking in the oil bath showed that active ingredient were present at the expected concentrations but did not enter the wood samples.
CONCLUSIONS & FUTURE WORK

FIRE-PROOFING
- maleinized oil grafted with THPC did not protect wood efficiently
- many technical problems occurred when working with grafted oils

Future development will focus on the formulation of more stable emulsions

BIOLOGICAL DURABILITY
- biocide-free blown and/or maleinized oil significantly reduced the risk for the wood of being decayed by insects and fungi
- oils added with biocides did not perform as good as expected
- interactions / inhibitions were suspected to occur between the oils and the biocides, lowering their uptake / efficiency

An understanding of these phenomena are necessary before selecting the more efficient biocides and scaling-up the process
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