Abstract: Royal process is a two stage wood-processing method; firstly the wood is preserved with a copper-based preservative system and then followed by hot oil treatment under vacuum for 3 hours. Royal treated wood products (garden furniture, cladding, terrace etc.) are used for exterior applications due to high dimensional stability and durability. New governmental restrictions, rising environmental and disposal concerns have resulted rapid global shift to copper-based systems. The aim of this study was to investigate potential alternatives for copper-based system used in Royal process. Lab scale experimental equipment for oil treatment was set up.

Key words: linseed oil, copper, chitosan, tannin, propiconazole, scots pine, CX-8

1. INTRODUCTION

Scots pine sapwood samples were impregnated with two different natural polymers and organic biocide – chitosan, tannin and propiconazole and a commercial copper salt preservative Wolmanit CX-8 as a control; afterwards impregnated samples were oil-treated with modified linseed oil. Two different preservative fixation parameters were performed. Preservative, oil retention and moisture content were calculated. The results indicated that 24 hour fixation time is needed. After leaching, specimens were exposed to fungal attack according to EN113. The fungal resistance of samples impregnated with natural polymers (tannin, chitosan) by using Royal process was improved. The results showed that Royal process works well with propiconazole. Eco-friendly improvement in Royal process was developed. Wood can be considered as one of the most sustainable materials. Wood is natural, renewable, recyclable and biodegradable, but untreated wood in outdoor exposure becomes easily subject to degradation by various causes such as different microorganisms, UV radiation and moisture. To prevent degradation, wood products are treated with different technologies – biocidal or non-biocidal systems. Major biocidal systems are water-borne copper-rich systems that contain complexed copper(II) and an organic co-biocide (e.g. Copper xyligen (CX), alkaline copper quat (ACQ) and copper azole (CA)). Non-biocidal methods include treating wood with various resins, polymers, oils, chemical modification, silanes and heat treatment [1]. Royal process is a wood processing method which combines wood preservation with biocidal system and subsequent non-biocidal treatment. In other words, wood is impregnated with water-borne copper-based preservative and afterwards treated with hot oil [2], [3], [4]. Modern copper-based preservatives are effective against fungi, but have lower fixation rate compared to chromate copper arsenate (CCA) and can easily be leached out during outdoor exposure conditions [5], [6], [7]. Royal process has a great environmental advantage; it significantly reduces the leaching of copper in use [4], [8]. New governmental restrictions and environmental concerns have resulted rapid
global shift to metal-based with non-metallic systems. For example, ongoing studies are investigating the use of organic biocides, natural polymers for nontoxic wood preservatives [14], [11].

Propiconazole is a derivate of triazole, an organic biocide, which was developed originally as agrochemical. Propiconazole is highly effective against fungi, leach resistance and biodegradable in the soil [1], [9]. Chitosan is a derivate of chitin, a natural polymer, which is manufactured primarily from waste products of crabs and shrimps. In recent years chitosan has received attention as a potential eco-friendly wood preservative [10], [11], [12].

Tannins are natural phenolic polymers, commercially produced from wood and barks. Several observations have shown fungicidal effect of tannins [13]. It is known that tannins show poor fixation. They accumulate on the wood surface and leach easily [14].

Wood destroying fungus causes serious damage to wood structures. Fungus requires four fundamentals to survive which are oxygen, favourable temperatures, moisture and nutrients. Decay fungi are divided into three types: soft-, white and brown rot.

The aim of this study was to investigate potential alternatives for copper-based system used in Royal process.

2. MATERIAL AND METHODS

2.1. Wood samples

Scots pine sapwood (Pinus sylvestris L.) blocks (50 x 25 x 15 mm) were selected, end-sealed and oven-dried at 103 ± 2°C for 24 hours. Absolute dry weight was recorded and samples were conditioned at 20°C and 65% relative humidity before impregnation.

2.2. Wood protection agents

Wood protection agents are presented in Table 1. The chitosan solution preparation, determination of the degree of deacetylation (FA) and the molecular weight (Mw) were examined by methods described by Larnøy [11]. Mimosa tannin powder was dissolved with deionized water without any additional chemicals.

### Table 1: Overview of used wood protection agents in this research

<table>
<thead>
<tr>
<th>Solution</th>
<th>Concent. [%]</th>
<th>Description</th>
<th>Active agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wolmanit CX-8</td>
<td>4.0</td>
<td>Commercial chromium free preservative based on copper and inorganic copper and boron compounds, pH = 9.5</td>
<td>Cu</td>
</tr>
<tr>
<td>Scanimp</td>
<td>5.1</td>
<td>Commercial microemulsion based on organic biocides. pH = 3.0</td>
<td>Propiconazole</td>
</tr>
<tr>
<td>Kitoflokk</td>
<td>5.0</td>
<td>Chitosan, natural polymer produced from crabs, pH = 5.3</td>
<td>D-glucosamine</td>
</tr>
<tr>
<td>Tannin</td>
<td>5.0</td>
<td>Water soluble polyphenol produced from mimosa bark, pH = 4.7</td>
<td></td>
</tr>
<tr>
<td>Oil</td>
<td>-</td>
<td>Modified linseed oil produced from flax plant seed, drying oil</td>
<td></td>
</tr>
</tbody>
</table>
2.3. Royal process
The Royal process includes two steps: impregnation procedure and following oil process.

2.3.1. Impregnation procedure
The impregnation procedure was identical for all solutions by using vacuum of 0.004 MPa for 30 min, and pressure of 0.9 MPa for 1 h. The samples were weighed to determine retention of solutions which was calculated by using the following Eq. 1

\[ R = \frac{G \times C}{V} \text{, } [\text{kg/m}^3] \]  

where G: \((T2-T1)\) is absorbed solution in sample in kilograms, C is concentration of solution, and V is volume of sample in cubic meters.

2.3.2. Oil process
In the second step the samples were treated with hot oil (modified linseed oil) at temperature 80°C in a vacuum (100 mbar) for 3 hours. Some seconds before the end of the process samples were pulled out from the oil and then air was released in afterwards in order to avoid high oil uptakes of the samples. Three sets of samples were run using 10 specimens for each set: 1) Samples were exposed to hot oil directly after impregnation; 2) Samples were stored 24 hours for fixation; 3) Samples without oil treatment were tested as controls. After the process, samples were dried at a temperature of 55°C and using 20 mbar vacuum until stabilization (7 days) to determine the oil uptake.

2.4. Decay test
The conditioned samples were leached according to the European standard EN84 (1997). After leaching, samples were vacuum dried. The specimens were exposed to fungi according to the EN113 (1996) using brown-rot fungi Coniophora puteana (CP) and white-rot fungi Trametes Versicolor (TV). The incubation time was 16 weeks at 22°C and 70% RH. After harvesting the samples were dried at 103 ± 2°C for 24 hours. Mass loss were calculated according to Eq.2.

\[ \text{Mass loss} (\%) = \frac{m_0 - m_1}{m_0} \]  

where \(m_0\) is the initial dry weight and \(m_1\) is the final dry weight after exposure to fungus.

3. RESULTS AND DISCUSSION
Before impregnation, the samples had mean moisture content 8.6 % with a standard deviation of 0.1 %.

3.1. Retention and oil uptake
Table 2 shows the retention of preservatives and oil. The average uptake for Wolmanit CX-8 was 25.2 ± 3.2 kg/m³, which is as twice high as the uptake achieved by a „Lowry process”[15]. It has been reported that average uptake of chitosan is 30 kg/m³, which is comparable with gained results in this study [16]. Samples directly exposed to hot oil after impregnation process had higher oil retention compared to samples with 24 hour fixation. According to previous studies of Royal process, the oil uptake increases with increasing fixation time. Higher oil uptake of wood samples without fixation could be explained by cracks that developed due to faster drying on end-sealed surfaces [3].

Table 2: Mean retention of solutions and mod. linseed oil

<table>
<thead>
<tr>
<th>Solution</th>
<th>Retention [kg/m³]</th>
<th>Treatment</th>
<th>Oil retention [kg/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CX-8</td>
<td>25.2 (3.2)</td>
<td>directly</td>
<td>151 (43)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24 h fixation</td>
<td>63 (25)</td>
</tr>
<tr>
<td>ScanImp</td>
<td>34.8 (1.2)</td>
<td>directly</td>
<td>207 (54)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24 h fixation</td>
<td>75 (17)</td>
</tr>
<tr>
<td>Kitoflokk</td>
<td>33.2 (4.4)</td>
<td>directly</td>
<td>110 (40)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24 h fixation</td>
<td>75 (29)</td>
</tr>
<tr>
<td>Tannin</td>
<td>32.1 (5.0)</td>
<td>directly</td>
<td>102 (37)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24 h fixation</td>
<td>62 (13)</td>
</tr>
</tbody>
</table>
3.2. Moisture content before and after Royal process
Moisture content after different oil treatments was significantly lower than it was expected (min 1.8 % ±0.5 % for CX-8 (24 h) treated with oil). Treated samples were all very dry and full of oil. Purpose for industry is to dry wood from wet stadium to a wood moisture content of 12 % – 20 % [3].

![Graph 1: Wood moisture content of Scots pine sapwood before and after oil process, SI – samples treated with Scanimp, Kito – Kitoflokk, Tan- tannin](image1)

3.3. Decay test
The mass loss during fungal exposure is displayed in Fig.4-7. Samples treated with CX8, Scanimp and their oil combinations showed less than 3% mass loss for both fungi species. According to other studies, chitosan and tannin have fixation problems [14]. This could not be proved by this study. However, chitosan treated samples without oil show poor protective properties when exposed to brown rot. Furthermore, tannin- and chitosan- treated samples without oil show poor protective properties against white rot. Chitosan and tannin samples treated in oil directly after impregnation with a wood protection agent and after 24 hour fixation showed very high antifungal effect against brown rot. However, chitosan and tannin treated samples without oil treatment showed low antifungal effect against white rot.

![Graph 2: Coniophora puteana](image2)

Fig.2.

![Graph 3: Coniophora puteana](image3)

Fig.3.

![Graph 4: Trametes versicolor](image4)

Fig.4.

![Graph 5: Trametes versicolor](image5)

Fig.5.

Fig 2-5: Mass loss of different treated and untreated wood samples after 16 weeks of exposure to brown rot (Coniophora puteana) and white rot (Trametes versicolor). U-untreated sample, US-virulence with end grain sealing, USW-virulence without sealing.
4. CONCLUSIONS

The two tested commercial wood preservatives alone or in combination with an oil treatment showed high resistance against fungal attack. The natural product chitosan showed low resistance against fungal attack. However, in combination with an oil treatment a high resistance against brown rot attack could be shown. In contrast, white rot attack could not be prevented with chitosan in combination with oil.

Wood samples treated with the natural product tannin and in combination with an oil treatment showed good antifungal properties when exposed to brown rot. However, white rot attack could not be prevented. Tannins and chitosan used as a wood protection agent in a Royal process, might be therefore not be suitable as an alternative to CX-8 in Royal process.

Scanimp provides high antifungal effectiveness and as an organic biocide could be an alternative product for copper-based products used in Royal process.

5. ACKNOWLEDGEMENTS

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