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The Fixation of New Alternative Wood Protection Systems by Means of Oil Treatment

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This paper focuses on the improvement of a combined impregnation process (CIP, also known as the Royal process). This treatment combines the protective properties of a wood protection agent and the hydrophobic properties of a subsequent oil treatment in a wood product. Copper-based wood preservatives, which are traditionally used in CIP, are very effective but their long-term future use is questionable because of environmental concerns, especially the toxicity against water-living organisms. There is a need for new environmentally friendly wood preservative systems for a use in CIP. The substitutes for copper used in this study are natural polymers and organic biocides. The aim of this research is to describe the fixation effectiveness of the following compounds: Chitosan, Propiconazole, Wolmanit CX-8, Tannin, fire protection agent, Alginate. The scots pine sapwood samples (50×25×15) mm were impregnated and oil treated. The treated products were analysed for their preservative-and oil-retention. Preservative fixation time influence on oil treatment was tested. The treated samples were leached according to EN84. Water samples were analyzed for the amount of active ingredient.

Keywords: chitosan, copper, EN84, propiconazole, scots pine, tannin.

1. INTRODUCTION

Untreated wood with low natural durability for exterior use becomes easily subject to degradation by various causes. Wood can be protected to increase service life and the most common method to protect wood is chemical preservation. CCA has been the major wood preservative more than 50 years for many applications but nowadays it is forbidden by governments.

Royal process was developed 30 years ago [1] which is a method for drying timber. It is also known as a combined impregnation process (CIP) because it combines the protective properties of a wood protection agent and the hydrophobic properties of a following oil treatment in a wood product.

Copper based preservatives have the widest distribution in Europe but it is known that they have a lower fixation rate than traditional chromate copper arsenate (CCA) [2, 3]. Wood preservation by combined impregnation process reduces the leaching of copper in use [4]. Copper based preservatives are very effective against attack by microorganisms but their long-term future use is questionable because of growing environmental requirements. For those reasons, preservatives based on organic biocides and natural polymers are considered as a good alternative as a substitute for a copper in wood preservation, also for use in CIP.

Chitosan is a nontoxic natural polymer, product of chitin, which is normally manufactured from crustaceans (shrimp, crayfish, crab), primarily waste product of food industry [5]. In recent years chitosan has received attention as a potential new eco-friendly wood preservative. Chitosan has proven to minimize fungal attack [6 – 17].

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Propiconazole is a derivate of triazole which was used as a fungicide in agriculture. Propiconazole is now as a main active ingredient in wood protection chemicals because of good antifungal effectiveness and nontoxic properties [18].

Tannins are natural water soluble phenolic or polyphenolic substances found in content in woody plants. Certain condensed tannins (proanthocyanidins) like “quebracho” and “mimosa” are produced commercially from woods and barks. Tannins have toxic effects against biotic factors; they may be preferred in use for protection of wood objects against destructive organisms [19 – 21].

The aim of this study was to investigate the potentials of some new alternative preservative systems for a use in combined impregnation process and to describe their fixation effectiveness.

2. EXPERIMENTAL

2.1. Wood samples

Samples of Scots pine sapwood *(Pinus sylvestris L.)* with dimensions (50×25×15) mm were end-sealed with two component sealer Pyrotect-2K-Aussen-Schutzlack 1720-7100-302 (Dreisol coatings GmbH) and treated in a two-step process and leached in water according to EN84.

2.2. Wood protection agents

The chitosan solution preparation, determination of the degree of deacetylation (F_A) and the molecular weight (*Mw*) were examined by methods described by Larnøy [13, 14]. Kitoflokk powder was dissolved in deionised water to a concentration of 5 % (w/v). With acetic acid to a pH range between 5 to 5.5. To reduce high viscosity after dissolving a 4 % (w/v) aqueous solution of potassium nitrite solution was added [22].

Table 1. Overview of used wood protection agents in this research

Solution	Description	pH	Concentration [%]	Reactive agent [%]
Kitoflokk	Natural polymer made of crabs (chitosan)	5.3	5.0	D-glucosamine (78 %)
ScanImp	Water soluble metal free micro emulsion based on organic biocides	3.0	5.1	propiconazole (1.45 %)
Tannin	Polymeric flavanoids made of plants (mimosa)	4.7	5.0	
Wolmanit CX-8	Chromium free preservative based on inorganic copper and boron compounds	9.5	4.0	copper (II) hydroxide carbonate (13.04 %)
Cecur	Fire protection agent	3.1		
Alginat	Natural polymer made of seaweeds	6.6		
Oil	Modified linseed oil from flax plant seed			

Mimosa tannin was solved in distilled water to a concentration of 5 % (w/v) without any additional chemicals.

2.3. Impregnation

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 equation:

$$R = \frac{G \times C}{V}\text{ , [kg/m}^3\text{]}, \tag{1}$$

where G: (T_2–T_1) is absorbed solution in sample in kilograms, C is concentration of solution, and V is volume of sample in cubic meters.

2.4. Oil process

The oil used in this treatment was modified linseed oil which is also used in industrial plants for CIP. Linseed oil is a drying oil and made from the seed of the flax plant *(Linum Usitatissimum)*. Precise overview of Royal process is described by Treu [23].

Three types of treatments were performed:

1. Wood protection agent (1 step) – all samples were impregnated with different solutions.
2. Wood protection agent and oil without fixation time (2 steps) – directly after impregnation wood samples were exposed to hot oil with a temperature of 80 °C, using a vacuum of 0.01 MPa for 3 hours. Some seconds before finishing the samples were pulled out from oil and air was released in.
3. Wood protection agent and oil treatment with 24 hour fixation time (2 steps) – after 24 hour fixation samples were placed to oil using same treatment as described above.

The samples were dried after Royal process using a vacuum 0.002 MPa with a temperature of 55 °C for 7 days in oven to determine afterwards the oil uptake.

2.5. Leaching Procedure

The conditioned weight of samples was taken before leaching. The wood samples were exposed to a vacuum of 0.004 MPa for 20 min and were left for 2 hours in the vessel. The water samples were collected according to EN84 [24].

The degree of fixation was calculated according to following equation:

$$FD = \frac{U - L}{U} \times 100\text{ , [\%]}, \tag{2}$$

where: FD is the degree of fixation [%]; U is the average uptake of copper and potential amount of leachable copper [kg/m³]; L is the leached out copper in oil related to the amount of wood [kg/m³].

2.6. Chemical analyses of the leaching water

Water samples were analyzed for the amount of main active ingredient. Tannin and fire protection agent leaching samples were not analyzed.

2.7. Determination of glucosamine and propiconazole by HPLC

The amount of glucosamine in the leaching water was determined by High Performance Liquid Chromatography (HPLC) [25]. Also the determination of propiconazole amount was analyzed by HPLC.

2.8. Copper analysis by ICP-AES

The determination of copper was performed by a simultaneous ICP-AES technique with axial or radial viewing of plasma on a Thermo Jarell Ash ICP-IRIS HR Duo [26].

3. RESULTS AND DISCUSSION

3.1. Drying process

Before impregnation the samples had a mean moisture content of 8.6 % ±0.1 %.

The solution uptake of wood samples in this study is generally significantly higher (25.2 kg/m^3 ±3.2 kg/m^3 for CX-8, 32.1 kg/m^3 – 34.8 kg/m^3 for other solutions) than compared to the solution uptake achieved by a Lowry process which is used in CIP. In industry the uptake of CX-8 is for pine wood 4 kg/m^3 (concentration 4 %). It has been reported by Larnøy [13] that average uptake of chitosan is 30 kg/m^3 which is comparable with gained results in this research (33.2 kg/m^3 ±4.4 kg/m^3).

Table 2. Uptake of used preservatives and oil

Treatment	Preservative uptake [kg/m^3]	Oil uptake [kg/m^3]
CX-8 + oil	25.2 (3.2)	151 (43)
CX-8 (24 h) + oil		63 (25)
ScanImp + oil	34.8 (1.2)	207 (54)
ScanImp (24 h) + oil		75 (17)
Kitoflokk + oil	33.2 (4.4)	110 (40)
Kitoflokk (24 h) + oil		75 (29)
Tannin + oil	32.1 (5.0)	102 (37)
Tannin (24 h) + oil		62 (13)

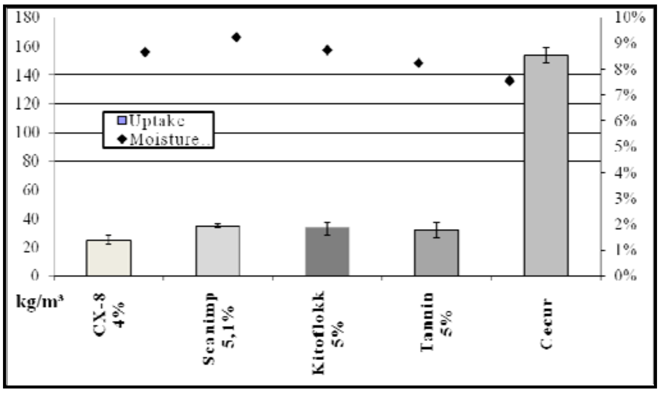


Fig. 1. Average uptake of different solutions in kilograms per cubic meter

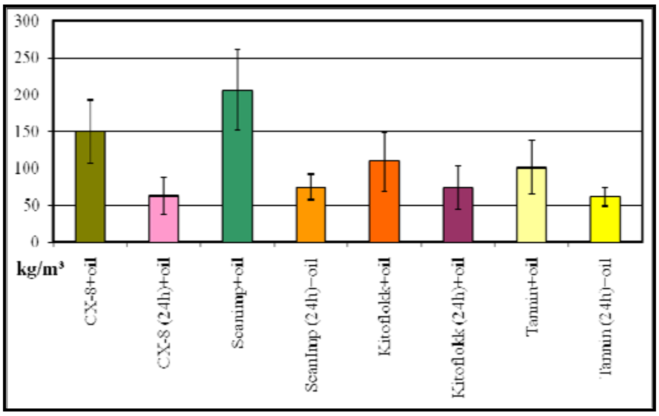


Fig. 2. Average oil uptake of Scots pine sapwood samples after different fixation time. The samples were treated 3 hours in hot modified linseed oil

3.2. Moisture content before and after combined impregnation 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 % [27].

Table 3. Wood samples moisture content before and after oil treatment

Treatment	Before [%]	After [%]
CX-8 + oil	138.7 (13.2)	7.2 (1.3)
CX-8 (24 h) + oil	72.1 (18.9)	1.8 (0.5)
ScanImp + oil	132.5 (9.5)	4.9 (3.2)
ScanImp (24 h) + oil	65.0 (10.8)	1.9 (0.6)
Kitoflokk + oil	135.7 (11.9)	47.1 (8.2)
Kitoflokk (24 h) + oil	78.4 (9.3)	15.6 (6.4)
Tannin + oil	131.7 (18.8)	4.4 (3.1)
Tannin (24 h) + oil	67.7 (18.0)	2.8 (0.6)

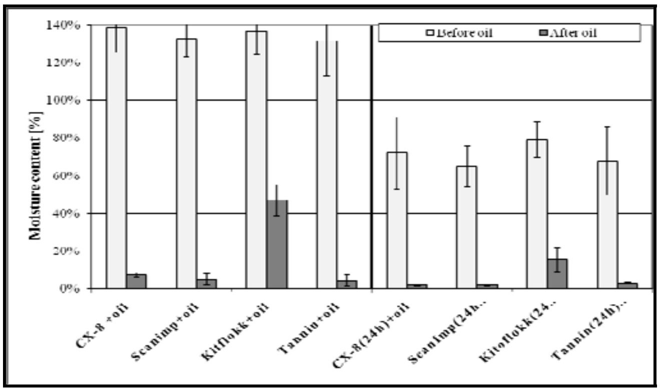


Fig. 3. Wood moisture content of Scots pine sapwood before and after oil process

All samples treated directly to oil were still foaming after 3 hours in hot oil. Samples treated with 24 hour fixation time did not have any foam in process after 3 hours, except samples treated with chitosan and fire protection agent.

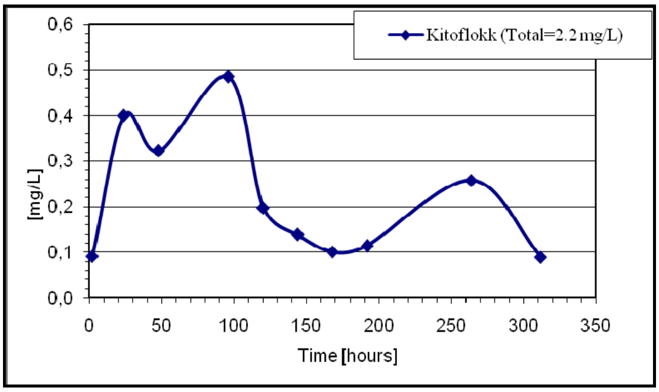
According to unpublished results has fire protection agent fixation problem. After oil drying process surfaces of samples were covered with small crystals. During the vacuum drying and leaching procedure a lot of oil and protection agent were leached out. Fire protection agents are not suitable for oil treatment. Therefore, the treatment was not further investigated. Also samples treated with tannin and alginate are not further described.

It has been studied whether or not copper impregnated wood samples leach copper during oil treatment. The impregnated wood samples do not leach a significant amount of copper during the oil treatment after different fixation times [27].

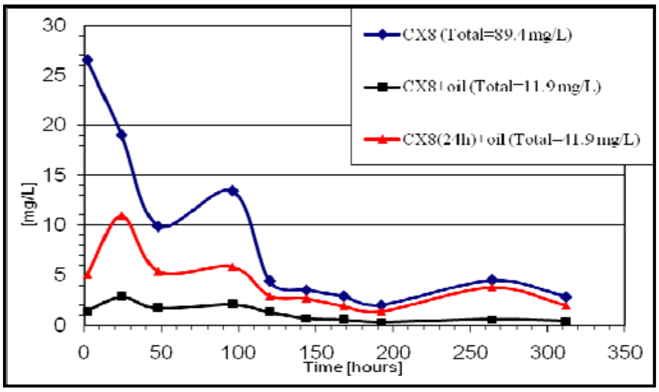
Glucosamine formula contains bonded H_2O which might be a reason for higher moisture content of samples treated with Kitoflokk after oil treatments (47.1 % directly in oil and 15.6 % after 24 h fixation). From medical research it is know that glucosamine helps bind water. More time in hot oil or longer fixation time needed for samples treated with chitosan.

3.3. Leaching

It is reported that CuHDO is fixed by approximately 75 % after 24 hours which is comparable with gained result (CX-8 FD = 75 %) [28]. All samples treated directly in oil after impregnation showed 2 % – 8 % higher degree of fixation than samples treated with 24 hour fixation time, except samples treated with Kitoflokk. Degree of fixation was calculated approx. 100 %. The amount of leached glucosamine is unexpectedly low. According to literature chitosan has a fixation problem but in the results there was no significant difference treated with oil or without. Leaching of propiconazole was reduced by oil treatment. It showed five times less leaching with an additional oil step than without oil (from 21.9 mg/L to 3.8 mg/L).



a



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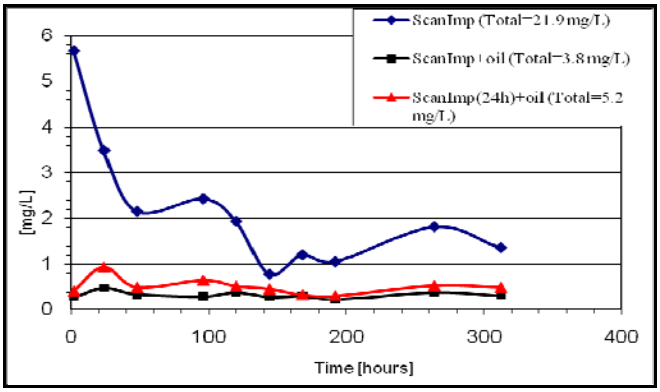

c

Fig. 4. Amount active ingredient in leaching water during 14 days leaching. Values for oil treated chitosan < 0.0001 mg/L are not shown in the graph: a – glucosamine, b – propiconazole, c – copper

Leaching of wood preservatives from impregnated wood products depends on a number of factors, such as wood, treatment and storage [29]. Directly oil-treated samples had twice higher moisture content before oil process and this is a reason for twice higher oil uptake and lower amount of leaching. According to Treu [27] there is no difference in the leaching prevention of copper based wood preservatives using different CIP treatments. This can be explained by the fact that these treatments resulted in a steady oil uptake.

4. CONCLUSIONS

Natural biocides and polymers used in CIP could be a good alternative to classical CIP because of lower toxicity and 24 h fixation time needed to gain lower uptake of oil.

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