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COMBINED EFFECTS OF COPPER AND OIL TREATMENT ON THE PROPERTIES OF SCOTS PINE WOOD

Due to its toxic effect on fungi, for the last 50 years copper has been one of the most widely used materials in the impregnation industry. The ban on CCA (copper-chrome-arsenic), known as an effective deterrent against fungi and insects, has led to the development of new and environmentally-friendly alternatives. Copper-azole (CuA), which is one of the most widely used of the newly-developed materials, is very effective against fungi and insects. However, one of its most serious problems is the fact that copper is leached from the wood. Various factors affect the leaching of copper from wood. One of the most important effects is the duration of fixation. In this study, samples impregnated with copper azole were exposed to a secondary impregnation process using tall oil and linseed oil 24 hours and 5 days, respectively, after the first impregnation. The effects of different fixation durations and oiled impregnation procedures on Scotch pine were investigated. For this purpose, biological, physical and chemical analyses of the wood were performed. Moreover, the amount of copper residual after leaching was also examined. According to the results obtained, it was observed that the duration of fixation had no significant effect on the physical properties, and that the linseed oil improved the physical properties of the wood. Through the copper and oil combination, an improvement in the physical and biological properties of the wood was observed, as well as a decrease in the amount of copper leached out.

Keywords: copper azole, tall oil, linseed oil, fungi test, leaching, XRF, FTIR-ATR

Introduction

Wood preservation by combined processes, including wood preservative treatment and a subsequent impregnation with a hydrophobic product, reduces the leaching of copper in use. When hydrophobic materials are used for impregnation, wood surface becomes hydrophobic and thus water uptake of wood decreases [Treu et al. 2011].

In wood protection, there is a trend towards the use of next-generation materials and methods, which includes utilizing recyclable materials and the by-

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-products of other industries. In recent years, there has been a growing interest in the use of natural and synthetic oils. In wood protection, various commercial or experimental oils are utilized. The most important ones of these are linseed oil, tall oil, orange oil, soybean oil, and nut oil [Ozgenç et al. 2013]. Tall oil is a by-product which derives from the production of paper from coniferous wood. It consists of resin acids (40-55%), fatty acids (40-60%) and unsaponifiable matter (5-10%). In some of studies, tall oil has been shown to decrease water uptake and to prevent fungal development. The large amount of oil required and the tendency for the oil to seep out of the treated wood have prevented the extensive utilization of tall oil [Hyvönen et al. 2006; Koski 2008; Lahtela 2014; Temiz et al. 2008].

Linseed oil, also known as flaxseed oil, is made from the pressing of the dried ripe seeds of the flax plant. The oil obtained is then exposed to a solvent extraction process in order to produce linseed oil. Linseed oil has some advantages, such as the fact that water left on the surface may penetrate given enough time and the oil finish continues to protect even as the wood expands and contracts. Linseed oil is generally composed of some oil acids. For example: α -linolenic acid (51.9-55.2%), palmitic acid (about 7%) and stearic acid (3.4-4.6%), oleic acid (18.5-22.6%), and linoleic acid (14.2-17%) [URL-2; URL-3]. Research indicates that linseed oil is water repellent and resistant to UV rays [Ozgenç et al. 2013].

In a study on ways to decrease copper leaching, it was reported that the hot oil procedure significantly decreased copper leaching and reduced the water uptake of wood samples during the weathering period. Moreover, it was emphasized that it was possible to obtain an aesthetic appearance by adding pigments to the oil, thereby decreasing colour change on the wood surface [Treu et al. 2011].

In this study, the effect of the fixation period, as well as tall oil and linseed oil, on copper leaching was examined. The amount of copper residual on wood samples exposed to the leaching process was measured. How the oils used in the impregnation process affected the physical properties of the wood was investigated via a water uptake test. Moreover, the effect of the executed procedures on the chemical and biological properties of the wood was examined.

Experimental methods

Material

Scots pine (*Pinus sylvestris L.*) logs were obtained from the Black Sea region of Turkey. Sapwood samples with dimensions of $5 \times 15 \times 30 \text{ mm}^3$ were used for the decay test, and samples measuring $20 \times 20 \times 10 \text{ mm}^3$ were used for the water uptake. The samples with a 30 mm diameter were used for XRF analysis as

shown in figure 1. The moisture content of the samples was approximately 12% prior to the experiments.

CuA was used as a wood preservative at a concentration of 2.4% on its own, as well as at the same ratio along with water repellents. The major constituents of the copper azole were copper carbonate (20.5%), 2-aminoetanol (< 20%), boric acid (< 5%), tebuconazole (< 0.5%), propiconazole (< 0.5%), polyethyleneimine (< 20%), organic acid (< 5%), and surfactant (< 5%).

The linseed oil and tall oil were provided, respectively, by the Izmir Altınyaz Company, Turkey, and by Çaycuma OYKA Paper Packing Company, also in Turkey.

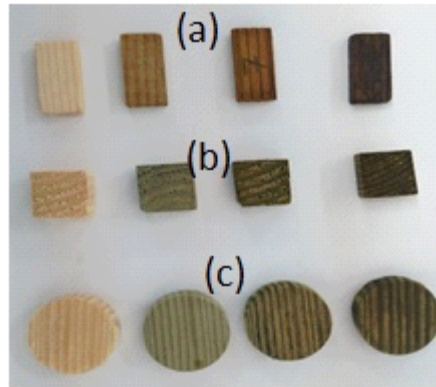


Fig. 1. Photographs of treated samples (a) decay test sample, (b) WA and TST sample, (c) XRF samples

Methods

After the samples were prepared, they were conditioned for the impregnation process at 65% relative humidity and a temperature of 25°C for 2 weeks. The air-dried samples were vacuum impregnated for 30 minutes at 650 mm Hg and under a pressure of 6 bars for 1 hour, as dictated by the ASTM D 1413-76 standard. The mass of the samples was measured before and after impregnation. The retention of the samples was determined using formula 1 given below.

$$\text{Retention} \left(\frac{\text{kg}}{\text{m}^3} \right) = \frac{G \cdot C}{V} \cdot 10 \quad (1)$$

where: G is the amount of preservative solution absorbed by sample (Mes - Meö) (g), C is the concentration of the preservative solution (%) and V is the sample volume (cm³).

The weight percent gain (WPG) which is indicative of the net oil uptake was determined from changes in the oven-dry mass after treatment using formula 2.

$$WPG(\%) = \frac{W_a - W_b}{W_b} \cdot 100 \quad (2)$$

where: W_b is the oven-dry mass of the specimens before treatment (g), and W_a is the oven-dry mass of the specimens after treatment (g).

The samples were divided into three test groups.

Test A: the examples in this group were impregnated with copper azole solution at a concentration of 2.4%.

Test B: the samples were firstly impregnated with CuA. After impregnation, the samples were left for 5 days at a temperature of 50°C and 24 hours under room conditions (25°C and 65% relative humidity) for fixation. After various fixation times, the second impregnation procedures were performed with 50% tall oil (50TO) and linseed oil (50LO). Ethanol was used in the preparation of the 50% tall oil and linseed oil formulation (tab. 1).

Test C: hot oil was used in this group. Initially, the samples were impregnated with CuA. After impregnation, the samples were left for 5 days at a temperature of 50°C and 24 hours under room conditions (25°C and 65% relative humidity) for fixation. Afterwards, the samples were placed in hot oil at 80°C, and then kept for 4 hours (tab. 1). At the end of this period, after which the samples were removed from the oil and cleaned, they were weighed in order to determine the increase in mass (equation 2).

In the samples to be exposed to the FTIR-ATR procedure, no leaching was performed. The sample groups are included in table 1.

Table 1. Sample groups

Control	Non treated
Test A	Treated with copper azole
	CuA1d+50TO (1 day fixation, 50% TO etc.)
Test B	CuA1d+50LO
	CuA5d+50TO
	CuA5d+50LO
	CuA1d+80TO
Test C	CuA1d+80LO
	CuA5d+80TO
	CuA5d+80LO (5 days fixation, 80 °C LO etc.)

The oven-dried wood specimens with dimensions of 20 × 20 × 10 mm³ were placed in a 300 ml beaker filled with deionized water. Six replicates were used in the treatment group. After 10 minutes, 1, 2, 3, 4, 24, 48, 168, and 336 h specimens were removed from the beaker and the excess water was removed by dabbing the surface with a tissue. After the dimensions and mass of the

specimens had been recorded, the specimens were again placed in the beaker and the water replaced. The test was continued for a total of 14 days. Relative water uptake (WA) and Tangential Swelling (TST) tests were calculated after each water replacement, according to formulas 3 and 4.

$$WA = \frac{W_2 - W_1}{W_1} \cdot 100 \quad (3)$$

$$DST = \frac{T_2 - T_1}{T_1} \cdot 100 \quad (4)$$

where: W_2 is the wet mass of the wood specimens after being soaked in water, W_1 is the initial dry mass, T_2 is the tangential dimension at any given time during the water-soaked condition and T_1 is the initial tangential dimensions of the specimen.

A decay test was carried out on both the leached and unleached specimens according to the principles of EN 113 [1996]. Leaching was conducted according to the AWPA 2000. E11-97 [2000] standard method, without stirring. The decay test for brown rot fungi, *Coniophora puteana* (Schumach.) P. Karst, was based on mini-block specimens on a 48 % malt extract agar in petri dishes. Six replicates were used for each test in the study as specified, with 12 control samples and 108 test samples. The treated and untreated samples were subjected to the decay test for eight weeks in a climate chamber with a temperature of 23°C and 70% RH. At the end of the exposure time, the mycelia coverings on the sample surfaces were removed and weighed. The samples were oven-dried at 103°C and reweighed. The mass loss was determined based on the dry mass before and after the decay test.

Fourier Transform Infrared Spectroscopy (FTIR-ATR) analysis was used to obtain information about the structure of the wood constituents and the chemical changes taking place in the wood impregnation process. FTIR spectra were obtained using a Shimadzu IRAffinity-1 equipped with a Single Reflection ATR pike MIRacle sampling accessory. Four accumulated spectra with a resolution of 4 cm⁻¹ were obtained for wavenumbers from 1100 cm⁻¹ to 1800 cm⁻¹ with 32 scans for each sample. The leaching procedure was not applied to the FTIR-ATR samples.

Via the X-Ray Fluorescence (XRF) technique, measurements can be taken rapidly, sensitively, reliably and at low cost, without damaging the material. For this reason, it is widely used in scientific and technological research. The samples prepared were cut to a diameter of 30 mm and a thickness of 5 mm. These samples were kept in a drying oven for 1 day at 60°C before starting the analyses and, in order to prevent any residual on the surface, they were air-dried with a 1 milibar air gun. On the same day, the samples were analyzed using an Epsilon 5 XRF device and the device's built-in software. The duration of the whole analysis was set at 25 minutes for each sample. Since the raw material

was cellulosic in origin, a $H_5C_{10}O_5$ balance was selected and the amount of elements on the surface was determined semi-quantitatively. The measurements were performed under a vacuum and He atmospheric conditions. The results were rapidly and reliably obtained at a concentration level of ppm-% without any damage.

Results and discussion

Water absorption (%), tangential swelling

After the impregnation of the Scots pine sapwood samples, the retention and percentage increases were measured, as shown in table 2. After impregnation with the copper, the retention values, accepted in the literature, were obtained for all the samples [Treu et al. 2011]. Generally, the WPG values showed an increase after the second treatment using linseed oil. The reason for using linseed oil more than tall oil ensues from the fact that linseed oil has a lower molecule mass than tall oil [BASF 2009; Panda 2008]. Moreover, the ratio of air bubbles in the oil hampers the penetration of the oil into the sapwood [Dizman et al. 2010]. The reason for the lower WPG values in the samples from test C compared with those from test B was due to the fact that the vacuum and pressure process was not used during the experiment. At the end of the five-day fixation period, in which the samples were treated with the oils, apart from the CuA5d+80TO, lower WPG values were obtained. In this study, the reason for this result may be that a 1 day oil impregnation may increase the amount of copper leached with oil. That is to say, samples impregnated with copper azole leached some amount of copper. On account of this, after 1 day's fixation, the samples treated with the oils had higher WPG values. According to one study, it was claimed that an increase in the fixation period was inversely correlated with the amount of leached copper [Treu et al. 2011].

The results for water absorption (%), and tangential swelling (%) of the treated wood samples are listed in table 2. The WA values of the control groups showed an increase from 44.98% to 114.72% after 336 h of exposure in water. However, the same WA values for the CuA groups were obtained with an increase from 25.56% to 134.54% after 336 h of exposure in water. The tall oil and linseed oil showed significantly lower WA results than the untreated (control) group. The results clearly show that the second treatment with oil significantly reduced the WA of the samples treated with oil. The best results were obtained with both the one day fixation time and 5 day fixation time in the samples impregnated with linseed oil.

A possible explanation for this could be the fatty acids in the linseed oil. Linoleic acid, one of the main acids in linseed oil has double C=C. When the bond is epoxidized, it becomes very reactive to the hydroxyl groups of wood and

Table 2. Water absorption (%), tangential swelling (%), retention (kg m⁻³) and weight percent gain (%) results for samples impregnated with copper azole and copper azole-oil

Treatment	Retention (kg m ⁻³)	Water Absorption (%)								
		10 min.	1 h	2 h	3 h	4 h	24 h	48 h	168 h	336 h
Control	–	44.98 (5.45)*	49.00 (3.59)	49.51 (3.48)	51.63 (3.37)	47.31 (2.25)	56.93 (4.63)	62.54 (7.05)	95.72 (9.88)	114.72 (10.03)
CuA	12.65	25.56 (2.30)	34.79 (2.54)	39.05 (2.06)	40.88 (2.18)	42.27 (2.08)	56.71 (3.41)	67.86 (3.81)	121.08 (6.39)	134.54 (8.25)
CuA1d+50TO	13.22 (30.14)**	6.93 (0.23)	12.54 (0.86)	17.23 (1.25)	20.83 (1.54)	24.34 (2.29)	39.09 (2.93)	42.44 (3.15)	58.62 (3.61)	69.19 (4.24)
CuA1d+50LO	15.21 (43.28)	4.49 (0.93)	8.96 (1.46)	11.17 (1.75)	12.77 (2.06)	14.51 (0.64)	22.89 (3.20)	24.90 (3.89)	31.90 (8.57)	35.30 (4.17)
CuA1d+80TO	12.92 (22.59)	7.69 (0.83)	16.42 (1.23)	21.85 (0.77)	26.24 (0.56)	29.49 (6.92)	45.13 (3.16)	51.96 (2.46)	75.34 (4.65)	89.23 (5.28)
CuA1d+80LO	13.16 (24.03)	8.15 (0.68)	16.84 (1.24)	23.99 (2.22)	29.15 (2.90)	32.35 (1.38)	45.52 (1.23)	49.55 (1.63)	71.69 (3.98)	81.94 (4.96)
CuA5d+50TO	13.80 (25.62)	9.03 (0.06)	15.26 (0.43)	20.27 (1.00)	24.01 (1.26)	26.80 (1.59)	37.89 (2.37)	44.33 (2.90)	58.55 (3.87)	65.98 (5.19)
CuA5d+50LO	14.12 (40.56)	4.92 (0.85)	9.15 (1.21)	12.35 (1.53)	14.26 (1.55)	15.90 (1.41)	23.74 (3.42)	26.41 (4.60)	35.21 (9.38)	36.93 (2.61)
CuA5d+80TO	13.94 (27.27)	9.14 (0.81)	16.12 (1.10)	21.68 (1.46)	25.44 (1.67)	27.12 (0.79)	40.26 (4.01)	47.20 (5.39)	64.31 (9.59)	70.18 (5.31)
CuA5d+80LO	12.63 (20.47)	10.28 (0.64)	18.61 (0.11)	25.51 (3.39)	30.21 (0.92)	33.60 (8.82)	48.13 (6.27)	56.99 (6.14)	80.49 (6.68)	98.16 (6.74)
		Tangential Swelling (%)								
Control	–	2.42 (2.02)*	5.22 (0.48)	5.28 (0.47)	5.53 (0.42)	5.56 (0.45)	5.88 (0.70)	6.24 (0.51)	5.72 (0.33)	6.18 (0.31)
CuA	12.65	4.47 (0.38)	4.40 (0.68)	4.48 (0.45)	4.47 (0.67)	4.59 (1.17)	5.05 (0.86)	5.00 (0.82)	5.08 (0.31)	5.70 (0.73)
CuA1d+50TO	13.22 (30.14)**	0.44 (0.20)	2.00 (0.25)	2.16 (0.14)	2.98 (0.35)	3.80 (0.35)	4.32 (0.25)	4.53 (0.51)	4.91 (0.26)	5.12 (1.06)
CuA1d+50LO	15.21 (43.28)	0.27 (1.03)	0.63 (0.47)	0.67 (0.12)	1.59 (0.60)	2.14 (0.66)	4.39 (0.71)	4.69 (0.58)	4.67 (0.44)	4.41 (0.71)
CuA1d+80TO	12.92 (22.59)	1.42 (0.06)	1.79 (0.33)	2.54 (0.82)	3.31 (0.82)	3.92 (0.99)	4.49 (0.94)	4.58 (1.13)	4.58 (0.74)	5.24 (0.77)
CuA1d+80LO	13.16 (24.03)	0.29 (0.33)	1.96 (0.19)	2.88 (0.56)	3.44 (1.12)	4.11 (0.90)	4.29 (0.38)	4.41 (0.44)	4.40 (0.40)	4.54 (0.82)
CuA5d+50TO	13.80 (25.62)	0.83 (0.08)	2.12 (0.20)	3.49 (0.05)	3.85 (0.25)	4.29 (0.34)	5.01 (0.58)	5.13 (0.85)	5.16 (0.20)	5.45 (0.46)
CuA5d+50LO	14.12 (40.56)	0.42 (0.22)	1.32 (0.01)	1.63 (0.29)	2.17 (0.29)	2.81 (0.25)	4.66 (0.11)	4.70 (0.28)	5.03 (0.61)	5.17 (0.53)
CuA5d+80TO	13.94 (27.27)	0.55 (0.36)	2.10 (0.25)	2.86 (0.37)	3.88 (0.46)	4.26 (0.66)	4.62 (0.46)	4.63 (0.57)	4.77 (0.34)	4.95 (0.48)
CuA5d+80LO	12.63 (20.47)	0.96 (1.86)	2.43 (1.09)	3.98 (1.00)	4.23 (0.57)	4.48 (0.65)	4.78 (0.77)	4.89 (0.81)	5.07 (0.79)	5.47 (0.66)

*Standard deviation within parentheses. **Weight percent gain (%).

thus absorption decreases. Due to oil treatment, the capillary water uptake is dramatically reduced by closing or filling the lumina in the wood. According to Hyvönen et al. [2006], the effectiveness of a water repellent treatment is probably dependent on both the amount of deposit and its precise location within the treated wood.

The tangential swelling of the control and CuA treated samples showed similar values but the second treatment with the oil significantly increased the initial tangential swelling. Yet, at the end of the 336 hour period, in the samples impregnated with the oil, lower tangential swelling values were recorded in comparison with the control. However, there was no remarkable difference between them. The reason for this may be that the oils in the sapwoods were leached over the course of time. The water, replaced with oil, lead to the expansion of the wood.

Decay test

The mass loss and moisture content of the wood treated with copper azole and copper azole-oil against brown rot fungi are shown in table 3.

Table 3. Mass loss (%), moisture content (%), retention (kg m⁻³) and weight percent gain (%) results for impregnated copper azole and copper azole-oil

Wood preservatives	Retention (kg/m ³)	WPG (%)		<i>Coniophora puteana</i>	
				mass loss (%)	moisture content (%)
CuA	17.49 (2.60)*	–	Leached	3.08 (1.30)	30.96 (3.83)
	19.29 (1.04)	–	Unleached	0.89 (0.88)	25.10 (1.73)
CuA1d+50TO	17.90 (1.27)	38.12 (2.26)	Leached	3.26 (1.71)	33.44 (4.37)
	20.48 (1.80)	40.92 (3.95)	Unleached	2.78 (0.87)	30.47 (5.79)
CuA1d+50LO	18.79 (1.78)	43.98 (5.40)	Leached	3.57 (1.69)	27.26 (2.24)
	18.33 (0.44)	48.51 (5.12)	Unleached	3.05 (1.02)	25.25 (6.82)
CuA5d+50TO	18.60 (1.53)	22.17 (2.00)	Leached	2.09 (1.92)	40.35 (7.89)
	18.07 (1.04)	21.34 (1.65)	Unleached	0.18 (3.41)	30.23 (3.63)
CuA5d+50LO	19.22 (1.07)	23.56 (2.87)	Leached	1.57 (1.33)	24.93 (0.99)
	18.35 (0.27)	22.97 (0.89)	Unleached	1.38 (0.26)	27.33 (1.17)
CuA1d+80TO	19.09 (2.14)	35.65 (3.19)	Leached	2.76 (1.60)	33.03 (3.59)
	18.56 (0.97)	35.15 (2.05)	Unleached	1.78 (2.08)	29.29 (4.65)
CuA1d+80LO	18.88 (0.83)	48.82 (2.69)	Leached	3.22 (1.21)	17.93 (6.04)
	17.71 (0.50)	43.91 (6.89)	Unleached	2.85 (1.67)	16.45 (2.84)
CuA5d+80TO	18.56 (0.47)	20.52 (1.76)	Leached	2.86 (1.07)	39.83 (5.79)
	18.09 (0.85)	20.09 (1.86)	Unleached	1.57 (0.71)	29.15 (8.82)
CuA5d+80LO	18.30 (0.40)	18.89 (3.60)	Leached	3.09 (0.97)	29.94 (3.36)
	17.81 (0.17)	20.32 (2.45)	Unleached	1.40 (0.54)	24.57 (3.75)
Control	–	–	Leached	16.00 (0.52)	65.66 (1.19)
	–	–	Unleached	11.78 (2.74)	54.21 (1.48)

*Standard deviation within parentheses.

All the treated samples had significantly lower mass loss than the untreated samples. The mass loss of the control (untreated) samples was higher than 20%, thus confirming the validity of the test according to EN 113 Standard [EN 113 1996]. The decay resistance of the treated wood samples with unleached CuA5d+50TO and CuA against brown rot fungi was very effective (less than 1% mass loss).

The impregnation agents, including copper, provide DNA modification and an interactive relation between the metal-enzymes owing to the formation of free radicals which remain as highly active as copper ions. The formation of highly reactive hydroxyl (OH⁻) radicals derives from the free cupric ions in motion within the system. These hydroxyl radicals may harm the protein molecules. Copper ion as a fungus (+2) may cause the generation of highly reactive free radicals which can harm the DNA and enzymes [Temiz et al. 2004]. A brown rot fungus completely destroys the carbohydrates in the secondary wall. Studies regarding the position of copper in the sapwood have shown that the concentration of copper is higher in the middle lamella and cell corners than in the secondary wall. Therefore, coppered impregnation agents inhibit the development of fungus [Freeman and McIntyre 2008]. Results in the literature are likely to confirm these results. The group samples from test A displayed quite a resistance against fungus. According to the results obtained, 0.89% of the mass loss was observed in the samples after 8 weeks. Humar et al. [2006] observed 28% loss of mass in control samples which were exposed to 8 weeks of fungus demolition, while the other samples, impregnated coextensively with CuCr and CuE, lost only 0.3-0.4 of their mass. Some amount of copper was leached, so fungus activity showed an increase due to the leaching of the copper.

The second impregnation with LO and TO slightly increased the mass loss caused by fungi decay, except in the case of CuA5d+50TO. However, the amount of mass loss did not conform to the criteria determined in the EN 113 standards. In other words, except for the case of CuA1d+50LO, in other variations the mass loss realized was under 3%. Due to the fact that tall oil clogs the lumens, the water can therefore provide repellency. As a result, this slows down fungus enzyme reactions [Schultz et al. 2007; Temiz et al. 2008]. According to the test results; the sample groups impregnated with LO for the second time suffered more loss of mass than TO. According to the literature, it was observed that the samples impregnated by 100% linseed oil suffered 15% of loss and the samples impregnated with tall oil suffered a 10% loss [Temiz et al. 2008; Yang and Calusen 2008].

There is a considerable amount of mass loss between the samples exposed to the leaching process and the samples which were not. The high standard deviations can be taken as the reason for this difference, because there is no direct relationship between the mass loss of fungus, the WA and the amount of leached copper (tab. 2 and 3).

The mass loss of the group samples from test C was greater than for those from the test B group samples, both of which were impregnated with oil in the same 5 day fixation periods. In the 1 day fixation, the group samples from test B suffered more loss of mass.

Fourier Transform Infrared Spectroscopy (FTIR-ATR)

The FTIR spectra of the treated and untreated samples are shown figures 2-3. Significant changes in the intensities of certain absorption bands are noticeable on the FTIR-ATR spectra between 1100 cm^{-1} and 1800 cm^{-1} . The assignments of the characteristic absorption IR bands of the wood samples in the fingerprint region are given in table 4.

Table 4. Assignments of IR absorption spectra bands in wood

Wavenumber (cm ⁻¹)	Functionality	Vibrating type
1740-1720	C=O in unconjugated ketones aldehydes and carboxyl	C=O stretching ¹
1660-1645	C=O in para-OH substituted aryl ketones, quinines	C=C stretching ³
1600	C=O in aromatic ring in lignin	Aromatic skeletal vibrations ²
1515-1500	aromatic ring	Benzene ring stretching vibrations ¹
1420	aromatic ring and CH	Benzene skeletal combined with C-H deformations ¹
1330-1240	CO in lignin and hemicellulose, and OH	C-O stretching and bending OH, antisymmetric stretching vibration of the acetyl ester groups ^{1,2}
1162-1086	C-O-C in cellulose	Antisym, Bridge oxygen stretching ²
1128	S-Syringyl lignin and C-O	C-H deformations in S lignin and C-O stretching ¹
1025-1035	C-O-C	Deformation ¹
897	Anti-symmetric out-of phase stretching in pyranose ring	Stretching in pyranose ring ¹

¹Ozgenç et al. [2013], ²Estevés et al. [2013], ³Temiz [2005]

In table 4, the peaks show deviations because of the translocations of the rings. In other words, the absorption peak at 1510 cm^{-1} is seen within the range of $1500\text{--}1515\text{ cm}^{-1}$.

Similar results are shown in figures 2 and 3: it can be seen that the treatment with copper and oil led to changes in the chemical structure of the wood. The peak at 1159 cm^{-1} changed after the treatment with copper and oils. These changes led to a decrease in copper and a significant increase in linseed oil. This

increase can be attributed to the ester bonds in the linseed oil [Ozgenç et al. 2013; Van der Weerd et al. 2005].

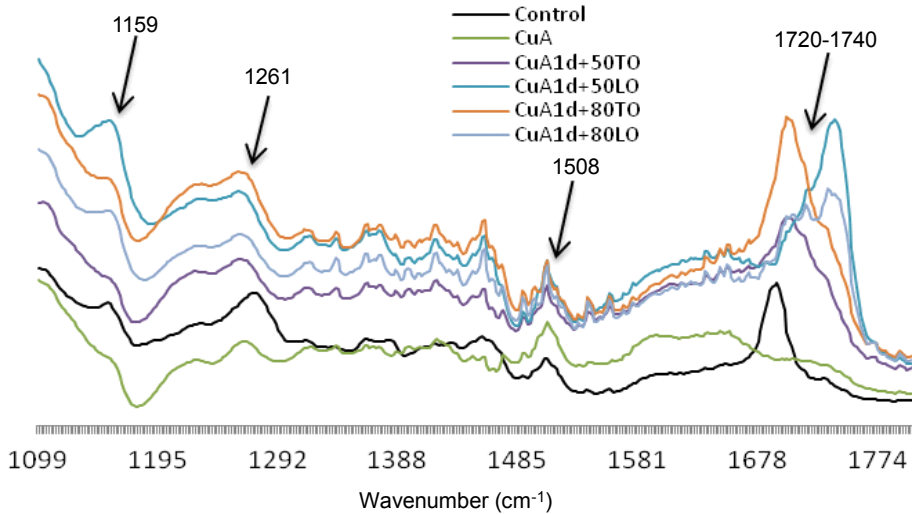


Fig. 2. FTIR-ATR spectra of the control, CuA and 1 day fixation time test group

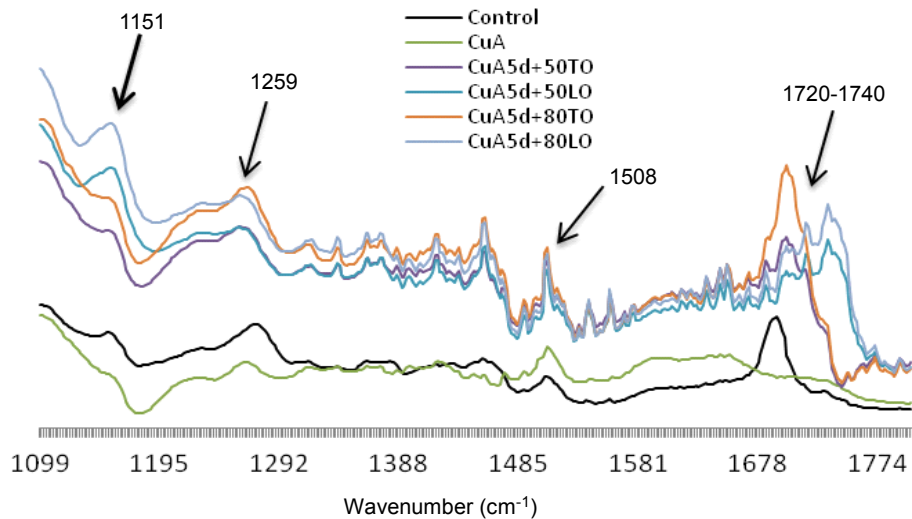


Fig. 3. FTIR-ATR spectra of the control, CuA and 5 day fixation time test group

The peak at 1261 cm^{-1} shows the CO and OH groups in the hemi-cellulose and lignin. A decrease was observed in the samples impregnated with the CuA solution. This decrease was minimized by using tall oil and linseed oil. The changes in the absorption peaks at $1230\text{--}1267\text{ cm}^{-1}$ are directly related to lignin delignification and modification of the aromatic rings. According to Temiz et al.

[2007], absorption peaks at around 1261 cm^{-1} for linseed oil and tall oil treatments do not change significantly.

The peak at 1508 cm^{-1} shows the aromatic ring peaks. In some studies, it was shown that the peak at 1508 cm^{-1} disappeared or significantly decreased after the impregnation procedure [Temiz 2005; Temiz et al. 2007; Salla et al. 2012]. Yet, in another study by Ozgenc et al. [2013], the increase in the peak at 1508 cm^{-1} was emphasized.

A decrease was found for the carbonyl absorption band at $1720\text{-}1740\text{ cm}^{-1}$, except in the case of the copper treatment. After copper impregnation, this peak disappeared. In their study carried out by using copper ethanol amine, Zhang and Kamdem [2000a], reported that the peak at 1739 cm^{-1} decreased after impregnation, and that this decrease was related to the anion of the carboxyl acid. Moreover, it was reported by Temiz [2005] that the fact that these peaks were not seen in the same region after impregnation is due to the effects of the impregnation materials on the translocation of the aromatic rings and from the interaction between the wood components and the copper. However, an increase was observed in the samples exposed to secondary impregnation with linseed oil and tall oil. The increase in the peak at $1720\text{-}1740\text{ cm}^{-1}$ during the treatment with the oils shares similarities with previous studies in the literature [Temiz et al. 2007].

X-Ray Fluorescence (XRF) Spectroscopy

The lowest amount of copper was found in the Cu5d+80TO treated wood. The highest amount of copper was obtained from the samples treated with CuA. A significant level of leaching (65%) was observed in the group samples from test A. In the study by Kangsepp et al. [2011], it was reported that after 14 days of leaching, 23 % copper leaching occurred in the samples impregnated with Tanalith-E.

The fixation duration is known to affect the leaching of copper. In this study, apart from CuA5d+50LO, the decrease in the amount of copper leached was inversely proportional to the increase in duration. The samples treated with oil kept at 80°C for the 5 day fixation period, and the impregnation executed at 50% concentration in the samples kept for the 1 day fixation, produced effective results.

In both the 1 day fixation and 5 day fixation periods, the lowest WA values were observed in the samples impregnated with linseed oil. However, the level of copper leached was lower in the samples treated with tall oil, apart from CuA1d+50TO (1490 ppm). 65% leaching was observed in the test A group samples. However, when the samples were treated with oil, the maximum leaching totalled 50.76 % (tab. 5). In the procedures in which the oils were used, the water uptake of the wood decreased and the copper leaching declined.

Table 5. The percentage of copper removed from CuA treated wood samples

Variation	Retention (kg/m ³)	WPG (%)	Initial Cu amount (ppm)	Total Cu amount leached out (ppm)	Percentage of Cu leached out (%)
CuA	15.94	–	4860	1920	65.31
CuA1d+50TO	18.78	28.18	5260	1490	39.52
CuA1d+50LO	14.56	30.03	3490	570	19.52
CuA1d+80TO	14.47	16.30	3220	960	42.48
CuA1d+80LO	14.03	12.36	3750	1180	45.91
CuA5d+50TO	14.25	25.75	5040	600	13.51
CuA5d+50LO	16.28	35.28	5970	2010	50.76
CuA5d+80TO	14.38	16.88	5320	320	6.40
CuA5d+80LO	17.03	18.68	6310	700	12.48

Conclusions

In this study, after 24 hours and 5 days of fixation, the physical, chemical and biological analyses of the samples previously treated with tall oil and linseed oil were performed. The results obtained are summarized below.

1. After the second process of impregnation with oils, the lowest water absorption and tangential swelling was observed in the CuA1d+50LO samples. The impregnation process carried out at 50% concentration had lower water absorption values than in the impregnation process conducted under 80°C.

2. According to the decay test results; a lower loss of mass was obtained in comparison with the control samples. This loss of mass was within the boundaries of the standards. The best results among the leached samples were obtained with the CuA5d+50LO. There was no statistical difference in terms of mass loss between the samples exposed to the 80°C heated oils and the samples impregnated in 50% concentration. Different kinds of fungus might be investigated in further research.

3. According to the FT-IR results, the intensities of the absorption band at 1508 cm⁻¹ (characteristic peak for lignin) were increased by the impregnation with copper, as well as linseed and tall oil treatments. A decrease was found for the carbonyl absorption band at 1720-1740 cm⁻¹, apart from the copper treated samples. This peak disappeared after the copper impregnation. The increase in the duration of fixation caused alterations in the chemical structure.

4. According to the study results, the level of copper leaching was higher. This rate decreased along with the use of the oils. The lowest level of copper leaching was observed in the test group C.

5. Before using samples impregnated with copper solutions, the fixation of the copper should be completed. In order to decrease copper leaching, oil-heat treatments are believed to be more efficient.

References

- ASTM D1413-76** [1994]: Standard test method for wood preservatives by laboratory soil-block cultures. In: ASTM. Annual Book of Standards, Vol. 4.10. Wood. American Society for Testing and Materials, West Conshohocken, PA, pp. 207-213
- AWPA 2000. E11-97.** [2000]: Standard method of determining the leachability of wood preservatives. American Wood Preservers' Association Standard
- Basf S.** [2009]: Polyol formed from an epoxidized oil. Patent no: WO2009138411 A1. Dated 19 October 2009
- Dizman E.T., Yıldız U.C., Can A.** [2010]: Treatment of Scots Pine wood with oil in water and water in oil emulsion systems: effects on boron leaching and water absorption. The International Research Group on Wood Protection. IRG/WP 10-30535
- European Standard EN 113** [1996]. Wood preservatives – Test method for determining the protective effectiveness against wood destroying basidiomycetes – Determination of toxic values. European Committee for Standardization (CEN), Brussels, Belgium
- Esteves B., Marques A.V., Domingos I., Pereira H.** [2013]: Chemical changes of heat treated Pine and Eucalypt wood monitored by FTIR. *Maderas Ciencia Y Tecnologia* 15 (2): 245-258
- Freeman M.H., McIntyre C.R.** [2008]: A comprehensive review of copper-based wood preservatives-with a focus on new micronized or dispersed copper systems. *Forest Product Journal* 58 (11): 6-27
- Humar M., Bucar B., Pohleven F.** [2006]: Brown rot decay of copper impregnated wood. *International Biodeterioration and Biodegradation* 58: 9-14
- Hyvönen A., Nelo M., Piltonen P., Niinimäki J.** [2006]: Using the emulsion technique and an iron catalyst to enhance the wood protection properties of tall oil. *Holz als Roh- und Werkstoff* 65: 247-249
- Kangsepp K., Larnoy E., Meier P.** [2011]: Leaching of commonly used impregnation agents affected by wood properties. In: Proceedings of the 7th meeting of the Nordic-Baltic Network in Wood Material Science and Engineering (WSE). October 27-28, 2011, Oslo, Norway
- Koski A.** [2008]: Applicability of crude tall oil for wood protection. Dissertation. University of Oulu
- Lahtela V., Karki T.** [2014]: Improving the UV and water-resistance properties of Scots pine (*Pinus sylvestris*) with impregnation modifiers. *European Journal of Wood and Wood Product* 72: 445-452
- Ozgenç Ö., Okan O.T., Yıldız Ü.C., Deniz I.** [2013]: Wood surface protection against artificial weathering with vegetable seed oils. *BioResources* 8 (4): 6242-6262
- Panda H.** [2008]: Handbook on tall oil rosin production, processing and utilization. Asia Pacific Business Press 106-E, Kamla Nagar, Delhi: 110-007
- Salla J., Pandey K.K., Srinivas K.** [2012]: Improvement of UV resistance of wood surface by using ZnO nanoparticles. *Polymer Degradation and Stability* 97: 592-596
- Schultz T.P., Nicholas D.D., Shi J.** [2007]: Water repellency and dimensional stability of wood treated with waterborne resin acids/TOR. Proceedings IRG Annual Meeting, IRG/WP 07-40364

- Temiz A., Yıldız U.C., Gezer E.D., Yıldız S., Dizman E.** [2004]: Interaction of copper based preservatives with wood. *Kafkas University, Artvin Faculty of Forestry Journal* 3-4: 204-211
- Temiz A.** [2005]: The effect of simulated weathering on preservative treated wood. Karadeniz Technical University, Science Institute, PhD thesis, Trabzon
- Temiz A., Terziev N., Eikenes M., Hafren J.** [2007]: Effect of accelerated weathering on surface chemistry of modified wood. *Applied Surface Science* 253: 5355-5362
- Temiz A., Alfredsen G., Eikenes M., Terziev N.** [2008]: Decay resistance of wood treated with boric acid and tall oil derivatives. *Bioresour Technology* 99: 2102-2106
- Treu A., Larnøy E., Militz H.** [2011]: Process related copper leaching during a combined wood preservation process. *European Journal of Wood and Wood Product* 69: 263-269
URL-2, <http://www.woodworkdetails.com/knowledge/finishing/linseed-oil> 22.12.2015
URL-3, http://www.vias.org/church_paintchem/church_paint_018_04.html 22.12.2015
- Van der Weerd J., Van Loon A., Boon J.J.** [2005]: FTIR studies of the effects of pigments on the aging of oil. *Studies in Conservation* 50 (1): 3-22
- Yang V.W., Clausen C.A.** [2008]: Inhibitory effect of essential oils on decay fungi and mold growth on wood. *AWPA* 103: 62-70
- Zhang J., Kamdem D.P.** [2000]: FTIR characterization of copper ethanolamine-wood interaction for wood preservation. *Holzforschung* 54 (2): 119-122

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