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The preliminary investigation on the use of impregnating formulations with organosilanes and glycerides in the wood treatment. Part I: AAS analysis and micrfungi test

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Abstract: *The preliminary investigation on the use of impregnating formulations with organosilanes and glycerides in the wood treatment. Part I: AAS analysis and micrfungi test*. The aim of the research was reactivity evaluation of organosilanes and wood or organosilanes+glicerides with wood. The silicone content in wood due to the impregnation reaction and silicone content in water extracts was determined by atomic absorption spectrometry (AAS). The results from the AAS analysis showed the used silanes as highly reactive with wood. In addition, biological test with the use of microfungi was performed on wood samples treated with selected organosilanes and glicerides. The results yielded by microfungi showed good fungistatic properties.

Keywords: organosilane, methyltrimethoxysilane, N-2-aminoethyl-3-aminopropyltrimethoxy-silane, atomic absorption spectrometry (AAS), monoglyceride, digliceride, microfungi.

INTRODUCTION

Organosilanes exhibit very high hydrophobicity caused by the presence of organic, mainly methyl, groups. As a result of reactions taking place between a silane molecule and wood the obtained wood exhibits considerably limited hydrophilic character and thus much reduced disadvantageous wood properties. Many wood properties, such as dimensional stability, hydrophobicity, weather resistance, fire resistance and strength, are improved by the application of organosilicone compounds (Tingaut et al. 2006; Sebe, De Jeso 2000; Sebe, Brook 2001; Sebe et al. 2004). The organosilicon compounds are also used as substances supporting antifungal properties of fatty acids derivatives. Esters of higher fatty acids or/and silane additives can contribute to the improvement of physico-chemical properties and decrease the risk of action of fungi (Hill 2004). There are wood impregnation agents [EP 1174231] which are based on resins which are reaction products of fatty acid anhydrides. An addition of one of the principal extractive constituents of pine wood, apart from fatty and resin acids, waxes, fatty alcohols, sterols and steryl esters are glycerides. Wood deprived of these constituents is characterised by significantly reduced resistance to biological attack. Performance and understanding mechanism of reactions between organosilanes and wood (Ratajczak et al. 2008) or its main component – cellulose was the main object of this study.

MATERIALS AND METHODS

Chemicals

The reaction of ethanol-based system containing organosilane (methyltrimethoxysilane (MTMOS) $CH_3Si(OCH_3)_3$ and N-2-aminoethyl-3-aminopropyltrimethoxysilane (AE-APTMOS) $NH_2(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$) with the mixture of monoglycerides and diglycerides of propionic acid and glicerol (MDG) was run at room temperature at different voluminal ratios. The homogenous wood material – scots pine sapwood (*Pinus sylvestris* L.) in the form of powder, was treated with silanes (1/25 w/v) at

room temperature at the simultaneous stirring with a magnetic bar stirrer for 2 h. Wood samples were left in working solutions at room temperature for next 2 h, then filtered and dried in air flow at room temperature. The obtained materials were leached using continuous extraction with deionized water at a constant ratio (1/100 w/v) for 2 h.

Atomic Absorption Spectrometry

Wood in the form of powder was treated with tested formulations and then extracted with water. The collected material was dried at room temperature. A representative sample of 0,5 g powder was collected from the prepared material. Samples were mineralized in a semi-closed microwave mineralization system Marsexpress CEM International. After each step of treatment wood samples were submitted for AAS analysis for silicon content using a Spectra 200 AA spectrometer by Varian. The final results were median values of three simultaneous measurements. Results repeated three times were characterized by very good compatibility. Before each assay analytical curves were prepared on the basis of a series of freshly prepared standard obtained from standard solution of silicon at a concentration of 1000 mg/dm^3.

Biological

The prepared systems were used to treat Scots pine samples in the shape of blocks with the dimensions: 0.5 x 4.0 x 4.0 cm (the last measurement along fibres) by soaking method for the period of 45 min. The preservative absorption was controlled and amounted to 240-280 g/m^2. Wood samples were exposed to microfungi. The spore suspension comprised of the following fungal species: *Aspergillus niger* (An), *Trichoderma viride* (TV), *Penicillium funiculosum* (Pf), *Paecilomyces variotii* (Pv). Evaluation of the efficacy was made by the visual assessment of fungal growth on the wood surface in accordance to ASTM D 5590-94 (table 1). Storage time of specimens exposed to microfungi at the temperature 28°C and relative humidity 80% was 21 days. Half of each series were subjected to artificial aging according to EN 84.

Tab. 1 Rating system for fungal growth acc. to ASTM D 5590-94

Index	Rating system
0H	no growth of fungi on the specimen, inhibition zone on the nutrient
0	no growth of fungi on the specimen
1	less than 10 % of the specimen area covered by fungi
2	less than 30 % of the specimen area covered by fungi
3	less than 60 % of the specimen area covered by fungi
4	specimen totally overgrown by fungi

Evaluation – a good fungicidal protection was given when there was no growth of fungi on the specimen

RESULTS AND DISCUSSION

Chemical analysis

Reactivity of organosilanes with wood powder is confirmed by the results of atomic absorption spectrometry.

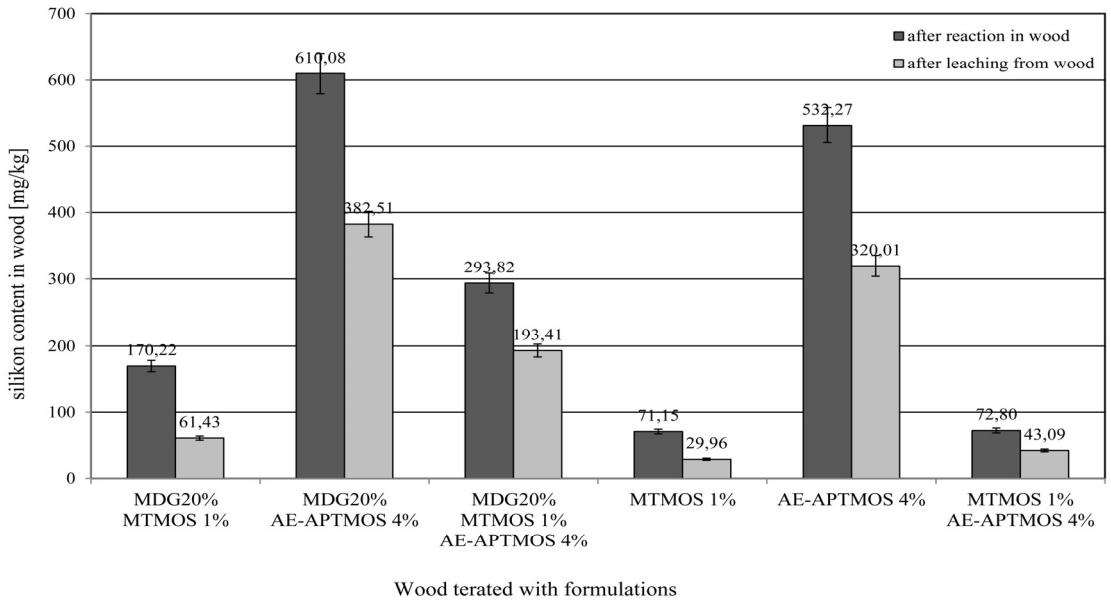

Fig. 1 Silicon concentrations in wood powder after reaction and in extraction solutions

Results of AAS analysis (silicone concentration) confirm a high reactivity of wood components with tested formulations. The highest values of silicon concentration in wood powder were assayed after reaction with the ethanol solution of N-2-aminoethyl-3-aminopropyltrimethoxysilane (AE-APTMOS) at 610 mg/kg. A very low percentage of silicon elution from wood, at its simultaneous high reactivity, is particularly evident in case of the system of 20% MDG/ 4% AE-APTMOS. This shows a permanent chemical bond between organosilane and wood, which was not broken in the process of hydrolysis.

Biological tests

The results of mycological investigations of Scots pine wood treated with the systems containing glyceride as well as glyceride and silico-organic compounds are presented in table 2.

Tab. 2 Silane formulations efficacy against microfungi

Silane	**Gliceride**	**Fungal growth (non leaching/leaching)***		
		I week	**2 weeks**	**3 weeks**
MTMOS 1%	-	4/4	4/4	4/4
AE-APTMOS 4%	-	2/4	4/4	4/4
MTMOS 1% + AE-APTMOS 4%	-	1/3	4/4	4/4
MTMOS 1%	20 %	3/4	4/4	4/4
AE-APTMOS 4%	20 %	1/3	2/4	4/4
MTMOS 1% + AE-APTMOS 4%	20 %	0/2	1/3	3/4
-	20 %	0/4	2/4	3/4

*The collected data comprise mean values from five samples subjected and five samples not subjected to aging processes

After 14 days of exposure to microfungi wood treated with silanes didn't show any strong antifungal properties. Wood treated with mixture of glicerides (at concentration 20%) showed enhanced durability against microfungi. However, the durability was not permanent when wood was subjected to ageing factors. Finally, a mixture of glicerides in glycerol and AE-APTMOS and MTMOS turned out as an effective formulation to protect wood against microfungi even after the exposure to ageing factors.

CONCLUSIONS

Low silicon concentrations in extraction solutions in comparison to high silicon concentrations determined in wood powder after reaction with organosilanes confirms the permanent character of the bond between wood powder and analyzed organosilanes. An addition organisilicon compounds reduce the leachability of glycerides from wood, and therefore applied systems have potential applications in compounds for the Use Class 3.

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Streszczenie: *Wstępne badania nad wykorzystaniem organosilanowo-glicerydowych preparatów do impregnacji drewna. Część I: analizy AAS i test biologiczne*. W pracy zbadano reaktywność drewna sosny zwyczajnej (*Pinus sylvestris* L.) z etanolowym systemem powłokowym na bazie MDG (mieszaniny mono- i diglicerydów oraz glicerolu), w zestawieniu z MTMOS (metylotrimtoksysilanem) i AE-APTMOS (N-2-aminoetylo-3 aminopropylotrimetoksysilanem). Analizę strukturalną drewna po reakcji z MGD i MTMOS oraz AE-APTMOS oraz po ekstrakcji wodą, wykonano metodą spektroskopii w podczerwieni (FTIR). Przedstawione wyniki analizy strukturalnej drewna z MTMOS i AE-APTMOS wskazują na wysoką reaktywność badanego organosilanu z substancją drzewną. Potwierdzeniem jest wysokie stężenie krzemu wykazane w analizie AAS. Bardzo niski procent wymycia krzemu z pyłu drzewnego, przy wysokiej jego reaktywności, jest szczególnie widoczny w przypadku mieszaniny: 20% MDG z udziałem AE-APTMOS o stężeniu 4%, jak również AE-APTMOS 4%/ MTMOS 1%. Ponadto zbadano aktywność biologiczną analizowanych systemów względem mikrogrzybów. Badania wykazały, że mieszanina MDG z AE-APTMOS i MTMOS wykazuje właściwości fungistatyczne także po procesach starzeniowych. Najwyższe wartości stężenia krzemu w pyle drzewnym oznaczono po reakcji z roztworem N-2-aminoetylo-3-aminopropylotrimetoksysilanu (AE-APTMOS), na poziomie 610 mg/kg. Wysokie stężenie krzemu w drewnie po ekstrakcji w porównaniu z wysokim stężeniem krzemu oznaczonym w pyle drzewnym po reakcji z organosilanami, potwierdza trwały charakter wiązania między drewnem a analizowanymi organosilanami.

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