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PERFORMANCE OF METHYL-TRIPOTASSIUMSILANOL TREATED WOOD AGAINST SWELLING IN WATER, DECAY FUNGI AND MOULDS

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ABSTRACT

Durability and dimensional stability of wood can be improved by various modification processes, including its treatment with silicones. Scots pine and Norway spruce sapwood specimens were treated by dipping method with 1, 5, 6.5, 10, 33 and 100 % water solutions of the ”Lukofob 39” (20 % of the methyl-tripotassiumsilanol and 19 % of additives including KOH). For modified specimens the following properties were determined: a) resistance against thickness swelling in tangential direction by standard ASTM D4446-08 (2008); b) resistance against wood-destroying fungi *Coniophora puteana*, *Serpula lacrymans* and *Trametes versicolor* by modified standard EN 113 (1996); c) resistance against moulds *Aspergillus niger* and *Penicillium* sp. by modified standard EN 15457 (2007). Laboratory studies showed that wood products modified with organo-inorganic-silanol substances could have an increased dimensional stability in water and a higher resistance to wood-damaging fungi.

KEYWORDS: Wood modification, organo-inorganic-silanols, swelling, decay fungi, moulds.

INTRODUCTION

Organosilicones are used as impregnates in several industrial applications, like concrete, brick, and stone protection, and also in the textile, paper and plastic industries (Simon et al.

2011). Modification of wood with these compounds is searched mainly with the aim to create water repellent and anti-weathering effects (Donath et al. 2006a, De Vetter and Van Acker 2010, De Vetter et al. 2010) and inhibit biodeterioration processes in its structural units (Donath et al. 2006b, Gosh et al. 2008).

The water repellent effect of organosilicones can be valued by more laboratory methods: a) water uptake methods; b) contact angle and surface tension methods; c) swelling and shrinkage methods (Simon et al. 2011). Their anti-weathering effect above ground can be determined by the L-joint method (De Vetter and Van Acker 2010) in accordance with the European standard EN 330 (1993). Anti-decay and anti-mould efficiency of wood products treated with organosilicones is important in their exterior or wet interior expositions and can be determined by more European standards, including EN 113 (1996) and EN 15457 (2007) which in a modified form have been used in this work.

From more kinds of organosilicones are for wood modification particularly effective the monomer silane molecules (e.g. alkyl-trialkoxy silanes) and the polymer silocone molecules. Small molecules of silanes well penetrate into wood structure (Donath et al. 2006a). However these molecules are not stable in wood and therefore firstly have to react with water molecules creating silanoles which are then reacted with –OH groups of wood (Hill 2006). Silicones are polymers used as water emulsions, which are not able to penetrate into cell walls of wood and after impregnation remain only in the lumina of wooden cells.

In this study, the anti-swelling, anti-decay and anti-mould effects of the water soluble organo-inorganic-silanol product Lukofob 39, which contains 20 % of the methyl-tripotassium silanol and 19 % of additives including KOH, were analyzed on the Scots pine and Norway spruce specimens. There was idea that in alkaline conditions at higher pH values the hemicelluloses of wood could be partly hydrolyzed and then easier entry into reactions with –OK groups of the organo-inorganic-silanol.

MATERIAL AND METHODS

Wood

From the sapwood of Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* Karst. L.) boards were prepared small specimens for the swelling test 6x38x254 mm (LxRxT), the fungal decay test 25x25x3 mm (LxRxT), and the mould test 50x10x5 mm (LxRxT). Specimens for the swelling test were firstly placed into conditioning room at a temperature of 23±2°C and relative humidity of 50±5 %, until they reached a constant weight $m_{before\text{-}treat.}$. Specimens for the mycological tests were firstly sterilized for approximately 6 hours at 103±2°C, and only then conditioned in sterile climatic room (t = 23±2°C; φ = 50±5 %) until a constant weight $m_{before\text{-}treat.}$.

Weighing of all specimens (i.e. before their treatment, after their treatment with silanol, before and after their fungal decay tests) was performed with an accuracy of 0.01 g.

Silanol

Modification of wood was performed with the Lukofob 39. It is a commercial organo-inorganic-silanol product of the Lučební závody a.s. Kolín in Czech Republic. This yellow-brown liquid have an alkaline character with pH of 13, solidifies at –10°C and its density is from 1270 to 1300 kg.m^{-3}. The Lukofob 39 contains 20 % of the silanol active ingredient (AI) – the methyl-tripotassiumsilanol ($CH_3K_3O_3Si$), and 19 % of additives (alkaline substance KOH and other non-volatile potassium compounds soluble in water, i.e. K_2O, K_2CO_3 and KCl).

In the experiments have been used water solutions of the Lukofob 39 in the following mass concentrations: C = 1, 5, 6.5, 10, 33 and 100 %.

Treatment of wood with silanol

The wood specimens were treated with water solutions of the Lukofob 39 by the dipping method at an atmospheric pressure of ≅ 100 kPa, temperature of 20±1°C, and immersion time of 3 minutes. After dipping, the excess water liquid present on specimen's surfaces could still penetrate deeper into wood over the next 5 minutes, and only then it was gently eliminated from wood surfaces with filter papers.

For treated wood specimens with known masses in wet state $m_{after\text{-}treat.}$, the retentions of the silanol active ingredient (AI) were calculated, i.e. the parameters of retention $R_{AI\text{-}Volume}$ in ($kg.m^{-3}$) and $R_{AI\text{-}Surface}$ in ($g.m^{-2}$) were computed by the Eqs. 1 and 2:

$$R_{AI\text{-}Volume} = [(m_{after\text{-}treat.} - m_{before\text{-}treat.}) / 1000 .\text{Volume of wood in } m^3]. [20.C/10000] \quad (1)$$

$$R_{AI\text{-}Surface} = [(m_{after\text{-}treat.} - m_{before\text{-}treat.}) / \text{Surface of wood in } m^2].[20.C/10000] \quad (2)$$

Finally, treated and control specimens were placed into conditioning room at a temperature of 23±2°C and relative humidity of 50±5 %, until they reached a constant weight $m_{clim.\text{-}after\text{-}treat}$.

Swelling test

The swelling tests were performed by the standard ASTM D4446-08 (2008), which use the Swellometer instrument (Fig. 1). Principle of this standard consists of comparing the thickness swelling of the treated wooden specimens ($S_{treat.}$) with thickness swelling of the control untreated ones ($S_{untreat.}$), both in the tangential direction (basic dimension of specimens was 254 mm). The anti-swelling efficacy of the silanol-treatments of wood (ASE or $AS_{relative}$) was evaluated in percentage (%) by the Eq. 3:

$$ASE = AS_{relative} = [(S_{untreat.} - S_{treat.}) / S_{untreat.}] . 100 \quad (3)$$

Fig. 1: Specimens inserted into the Swellometer instruments.

Every pair of Scot pine and Norway spruce specimens for testing in the Swellometer was formed by two bordering slices from a parent board. One specimen of the pair was treated with the silanol and the second one remained untreated (control - reference specimen). For one treatment process five pairs of specimens (i.e. together 10 specimens) were tested, and each of the pairs was prepared from a different parent board.

The treated and control specimens inserted into the Swellometer instruments were placed into a container with distilled water and maintained at 24±3°C (75±5°F) for 30 minutes. Each specimen was completely submerged in water, but on the other hand, the dial and dial stem stayed dry. The tangential thickness swelling was noted from the dial after the 30-minute period.

Fungal decay test

The anti-decay resistance of the silanol-treated Scots pine sapwood specimens was searched against two brown-rot fungi *Coniophora puteana* (Schumacher) P. Karsten and *Serpula lacrymans* (Wulfen) J. Schröt, and against one white-rot fungus *Trametes versicolor* (L.) Pilát [Synonym: *Coriolus versicolor* (Linnaeus) Quélet]. Fungal decay tests were based on the EN 113 (1996) with some modifications as follows: - using of specimens with a smaller dimension of 25x25x3 mm (LxRxT) instead of 50x25x15 mm (LxRxT); - treatment of specimens by dipping instead of their vacuum impregnation; - shorter time of fungal test in accordance with Chittenden and Singh (2011), so only 6 weeks instead of 16 weeks; - exposure of specimens in Petri dishes with a diameter of 100 mm instead of in a 1-liter Kolle's flasks. After 6 weeks, the specimens were pulled out from Petri dishes, cleaned carefully with the aim to remove any adhering mycelium, gently air-dried during 4 days, and finally conditioned in the climatic room at 23±2°C and 50±5 % relative humidity until they achieved a stable weight $m_{clim\text{-}decayed.}$.

The anti-decay resistance tests were valued on the basis of specimen's mass losses in percentage (%) by the Eq. 4:

$$\Delta m = [(m_{clim.\text{-}after\text{-}treat.} - m_{clim.\text{-}decayed}) / m_{clim\text{-}after\text{-}treat.}].100 \qquad (4)$$

Mould test

The anti-mould resistance test of silan-treated Scots pine sapwood specimens 50x10x5 mm (LxRxT) against moulds *Aspergillus niger* Tiegh. and *Penicillium* sp. was based on the European Standard EN 15457 (2007) with some modifications in the sterilization process and the shape of specimens. UV light sterilized specimens were placed into Petri dishes with a diameter of 100 mm (two pieces into one dish filled with 3 – 4 mm thick layer of the malt-agar), and then inoculated with water spore suspensions of tested moulds. Incubation of specimens lasted 4 weeks at a temperature of 24±2°C and relative humidity of 90 – 95 %.

The anti-mould resistance of specimens was assessed visually on their top-side 50x10 mm in the 7, 14, 21 and 28th day, using the mould activity (MA) scale from 0 to 4, i.e., 0 = no mould; 1 = mould up to 10 %; 2 = mould up to 30 %; 3 = mould up to 50 %; 4 = mould more than 50% on the surface.

RESULTS AND DISCUSSION

Retention of silanol

The volume and surface retentions of the active ingredient (AI) – the methyl-tripotassiumsilanol molecules present in the Lukofob 39, into the pine and spruce sapwood specimens are in Tab. 1. However, due to possible selective uptakes caused by chromatographic effects at transport of the water silanol solutions in wood, the gravimetrically determined retentions can not demonstrate distribution of the silanol molecules in wood structure.

The volume retentions $R_{AI\text{-}Volume}$ in kg.m^{-3} were higher for specimens used for the swelling test in tangential direction (6x38x254 mm = LxRxT) in comparison to smaller specimens used for the decay test (25x25x3 mm = LxRxT). This result can be explained by a very small length in longitudinal direction and then by a higher portion of axial surfaces at specimens used for swelling test.

For specimens used in the swelling tests, which length in the longitudinal direction was only 6 mm, the Norway spruce sapwood occurred partly better permeable comparing with the Scots pine sapwood. This unforeseen result is not in a good correspondence with knowledge published by Siau (1988), Kurjatko and Reinprecht (1993), and more other researchers, however, it can be explained by a specific shape of used specimens which length in the longitudinal direction was approximately only 2-times bigger than length of tracheids.

Tab. 1: Retentions of the silanol active ingredient (AI) present in the Lukofob 39 into wood specimens used subsequently for the swelling and mycological tests.

Silanol		Retention of the silanol active ingredient (AI) into wood specimens			
		Swelling test		Decay test	Mould test
Lukofob 39 (%)	AI (%)	Scots pine $R_{AI\text{-}Volume}$ ($kg.m^3$)	Norway spruce $R_{AI\text{-}Volume}$ ($kg.m^3$)	Scots pine $R_{AI\text{-}Volume}$ ($kg.m^3$)	Scots pine $R_{AI\text{-}Surface}$ ($g.m^{-2}$)
1	0.2	0.42 (0.01)	0.46 (0.01)	-	-
5	1.0	1.98 (0.14)	2.37 (0.08)	-	-
6.5	1.3	2.57 (0.25)	3.08 (0.09)	0.73 (0.17)	0.88 (0.19)
10	2.0	3.94 (0.39)	4.64 (0.49)	1.44 (0.39)	1.60 (0.31)
33	6.6	9.63 (0.80)	14.26 (1.03)	6.86 (1.28)	7.85 (0.91)
100	20.0	34.97 (1.83)	46.68 (1.59)	25.60 (3.10)	31.54 (2.92)

Note: The Lukofob 39 contains 20 % of the methyl-tripotassiumsilanol.
Numbers in parentheses are the standard deviations.

Anti-swelling efficiency

The anti-swelling efficiency of the Lukofob 39, or of its silanol active ingredient (AI), was examined for its water solutions from 1 to 33 % and also for the 100 % undiluted concentrate (Tab. 2, Fig. 2). The tangential swelling of specimens 6x38x254 mm (LxRxT) proportionally decreased, or the relative anti-swelling efficiency $AS_{relative}$ (ASE) values proportionally increased, with increase in the amount of the silanol molecules in wood specimens.

The anti-swelling efficacy of the Lukofob 39 was demonstrated already from its 1 % concentration, and its 100 % concentration has resulted in the anti-swelling efficiency greater than 65 %, both for Scots pine and Norway spruce. The high anti-swelling effect of this organo-inorganic-silanol product can be explained either by penetration of its molecules into wood cell walls connected with more or less durable blocking of –OH groups in hemicelluloses, cellulose and lignin, and also by filling of cell lumina connected with a time extension of water sorption processes during the swelling test. However, for a practice have to be recalled that the high $AS_{relative}$ (ASE) values achieved in laboratory test will be for a real wooden product with higher cross-sections (façade tiles, etc.) probably smaller due to smaller penetration of this modification agent from their radial and tangential surfaces.

Tab. 2: Relative anti-swelling efficiency ($AS_{relative}$) of the silanol active ingredient (AI) present in the Lukofob 39 valued in the tangential direction for the Scots pine and Norway spruce specimens.

Silanol		**Swelling test**	
Lukofob 39 (%)	**AI (%)**	**Scots pine $AS_{relative}$ (%)**	**Norway spruce $AS_{relative}$ (%)**
1	0.2	4.4 (2.2)	8.5 (4.9)
5	1	13.6 (5.9)	21.2 (4.0)
6.5	1.3	15.5 (5.2)	23.8 (3.1)
10	2	16.5 (6.7)	27.0 (8.2)
33	6.6	28.8 (5.5)	36.5 (4.3)
100	20	69.4 (3.3)	74.3 (4.0)

Note: The arithmetic mean values are from 5 treated and 5 control replicates, according to ASTM D4446-08 (2008). Numbers in parentheses are the standard deviations.

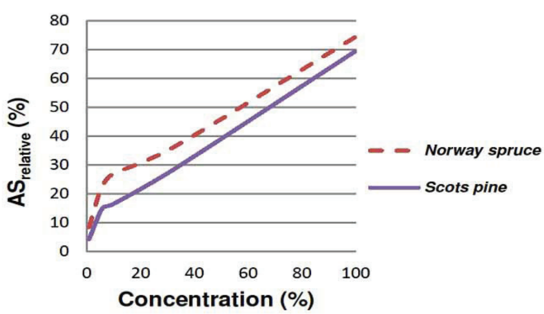


Fig. 2: Relative anti-swelling efficiency ($AS_{relative}$) of the Norway spruce and Scots pine specimens increased with higher concentration of the Lukofob 39.

Anti-decay efficiency

The Lukofob 39 evidently increased the anti-decay resistance of the Scots pine specimens (Tab. 3, Figs. 3 and 4). Mass losses of the silanol-treated pine wood decreased in accordance with increased portion of the active ingredient (AI). However, at explanation the anti-decay efficiency of the Lukofob 39, there should be taken into account either its alkaline character with high pH values from 11.5 (for the 6.5 % water solution) to 13.0 (for the 100 % concentrate), caused especially by presence of the alkaline additive KOH. On the other hand, the pH value of the untreated pine sapwood was only 5.3.

The anti-decay efficacy of the silanol product Lukofob 39 was more pronounced against the brown-rot fungi *Serpula lacrymans* and *Coniophora puteana*, and less significant against the white-rot fungus *Trametes versicolor* (Tab. 3, Fig. 3). This knowledge is evident also from the exponential equations between the mass losses of decayed specimens "Δm" and the increased concentrations of the Lukofob 39 used in modification processes, when its concentration "C" was from 0 to 100 %. For these exponential equations were determined quite high correlation coefficients (R) – Fig. 3.

Tab. 3: Mass losses of the Scots pine sapwood specimens treated with the Lukofob 39 after attack with the wood-destroying fungi Coniophora puteana, Serpula lacrymans and Trametes versicolor.

Silanol		Decay test – mass losses caused by fungi (%)		
Lukofob 39 (%)	**AI (%)**	***Coniophora puteana***	***Serpula lacrymans***	***Trametes versicolor***
Control	-	24.1 (4.4)	31.1 (6.7)	13.4 (3.7)
6.5	1.3	18.6 (3.9)	18.9 (3.2)	11.6 (1.9)
10.0	2.0	16.2 (4.4)	12.7 (3.0)	10.5 (1.8)
33.0	6.6	10.1 (2.4)	9.0 (3.0)	9.2 (2.3)
100	20	7.6 (1.2)	5.9 (2.4)	9.7 (1.1)

Note: The arithmetic mean values of treated specimens are from 5 replicates, and of control ones from 20 replicates. Numbers in parentheses are the standard deviations.

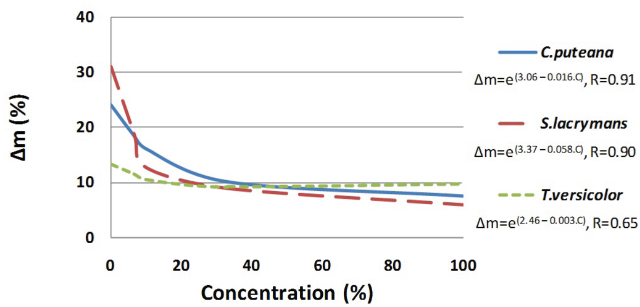


Fig. 3: Mass losses (Δm) of the Scots pine sapwood specimens after 6-weeks decay tests evidently decreased (preferentially at action of the brown-rot fungi C. puteana and S. lacrymans) with higher concentration of the Lukofob 39.
Note: Curves in the Fig. 3 were modelled by an exponential relation $\Delta m = e^{(a - b.C)}$*, as well (see text).*

Coniophora puteana *Serpula lacrymans* *Trametes versicolor*

Fig. 4: Strong fungal attack of the control Scots pine sapwood specimens (K – in left), and inhibited fungal attack of the silanol-treated ones at using the 100 % Lukofob 39 (L4 – in right) – photos after 6 weeks.

Anti-mould efficiency

The anti-mould resistance of the silanol-treated Scots pine sapwood specimens was higher than the control ones (Tab. 4, Figs. 5 and 6).

Tab. 4: Mould attacks of the Scots pine sapwood specimens treated with the Lukofob 39.

Silanol		**Mould test – mould attack from 7th to 28th day (0-4)**							
Lukofob39 (%)	**AI (%)**	***Aspergillus niger***				***Penicillium* sp.**			
		7th	**14th**	**21th**	**28th**	**7th**	**14th**	**21th**	**28th**
Control	-	4	4	4	4	4	4	4	4
6.5	1.3	0	1.67	2.33	3	3	4	4	4
10.0	2.0	0	1.5	2.5	2.67	2	2.5	3.17	3.5
33.0	6.6	0	1.17	2.17	2.67	1	1.83	2.67	3.17
100	20	0	0.83	1.17	2.33	0	0.17	0.33	1.17

Note: The arithmetic mean values of treated and control specimens are from 6 replicates.

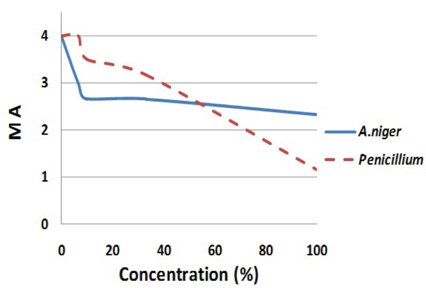
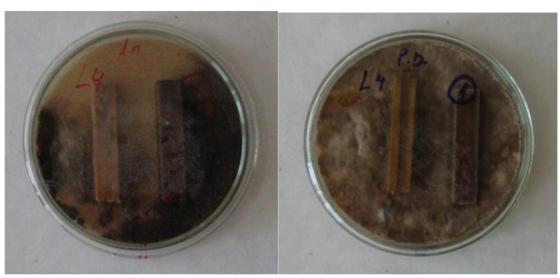


Fig. 5: Mould attacks (MA) of the Scots pine sapwood specimens decreased with higher concentration of the Lukofob 39 – results from the final 28th day.



Aspergillus niger *Penicillium sp.*

Fig. 6: Strong mould attack of the control Scots pine sapwood specimens (K – in right), and partly inhibited mould attack of the silanol-treated ones at using the 100 % Lukofob 39 (L4 – in left) – photos from the final 28th day.

Mould attacks, caused by the *Aspergillus niger* and *Penicillium* sp. microscopic fungi, were intensively inhibited to the end of the first week, and milder inhibited to the end of the third week. However, after four weeks the surfaces of the silanol-treated specimens have been already evidently covered with mycelia of both mould species. Only at using the highest 100 % concentration of the Lukofob 39 the surfaces of wood more apparently resisted to the *Penicillium* sp. The anti-mould effect of this organo-inorganic-silanol product can be explained not only by the presence of its molecules in surfaces of wood specimens, but also by its alkaline character (pH from 13.0 for the 100 % solution to 11.5 for the 6.5 % solution).

CONCLUSIONS

- The anti-swelling efficacy of the organo-inorganic-silanol commercial product Lukofob 39 (20 % of methyl-tripotassiumsilanol, and 19 % of additives) has been evidently demonstrated from its 5 % concentration. Application of the undiluted product (100 % concentration) has resulted in the anti-swelling efficiency greater than 65 %, both for Scots pine and Norway spruce.
- The anti-decay efficacy of the Lukofob 39 appeared already at its 6.5 % concentration, and further exponentially increased till its 100 % concentration. This silanol product mostly supressed growth of the dry rot fungus *Serpula lacrymans*, less of the cellar fungus *Coniophora puteana* (both belong to brown-rot fungi), while its inhibition effect against the many-zoned polypore white-rot fungus *Trametes versicolor* was only a negligible.
- The anti-mould efficacy of the Lukofob 39 against the *Aspergillus niger* and *Penicillium* sp. microscopic fungi was seen especially at the beginning of mycological tests. However, its highest 100 % concentration against the *Penicillium* sp. was significantly effective also in the final 28th day.

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