Durability of Epoxi-Oil Modified and Alkoxysilane Treated Wood in Field Testing

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Increased interest in oils and silicones as hydrophobic agents creates the need for testing, with the aim of better understanding their field performance and preparation for an eventual market entrance of these products. This study reveals the aboveground test performance of wood impregnated with epoxidised linseed oil (ELO) and organofunctional alkoxysilanes and compares the achieved results with the significantly more severe inground exposure and initial laboratory tests. Since ELO and siloxanes are not active ingredients, they were combined with fungicides for better performance. Various oil and alkoxysilane retentions and combinations with boric acid, organic fungicides, and creosote were impregnated in wood and tested. Untreated, chromium-copper-arsenate (CCA)-treated and thermally modified samples served as references. Long-term aboveground and inground testing of the studied formulations enforced the conclusion that ELO combined with biocides is suitable protective formulation for timber in both above- and in-ground exposure. Two alkoxysilanes were more effective in timber exposed aboveground. No decay was registered in the ELO and alkoxysilane treated lap-joint samples, while the untreated controls were close to failure after five years of exposure.

Keywords: Alkoxysilane; Epoxidised linseed oil; Boric acid; Hydrophobisation; Wood durability

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INTRODUCTION

Wood protection has passed through a significant metamorphosis, starting from the use of highly toxic formulations containing arsenate at high concentrations to using formulations based entirely on copper. Organic-based preservatives, chemically modified wood, and thermally modified wood have also been introduced on the market in the recent decades. Arsenate is obsolete; chromium and boron compounds are still in use but subject to intense debate regarding the environmental and health consequences of their further use. Creosote is another wood preservative that could be banned soon. Known for more than two centuries, creosote still has a restricted but irreplaceable role in the protection of wooden poles and railway sleepers. The price of creosote has doubled in the recent years. In some countries, *e.g.*, Sweden, an additional tax on creosote may be introduced soon. In Europe, the use of creosote is permitted until 2018; its further use is debatable and uncertain.

The above offers a good reason for research and development of formulations and methods that are less harmful for the environment and can eventually substitute for the creosote as well as provide new alternative protection for wood in- and aboveground. The existing and allowed alternatives are few and comprise impregnation of wood preservatives

containing copper and organic biocides, double impregnation with copper formulations and hydrophobic substances (*e.g.*, oils), development of mechanical barriers (*e.g.*, pole bandages and boots for in-ground exposure), and some chemical modification methods (acetylation and furfurylation).

The present study is dedicated to testing of alkoxysilanes and epoxidised linseed oil (ELO), alone or in combination with organic biocides for the protection of wood exposed in- and aboveground. Based on a great number of investigations that revealed the possible use of plant oils for wood protection, a conclusion was drawn that the main effects of plant oils and tall oil (a by-product from chemical pulping of resinous softwoods consisting of 40 to 60% fatty acids, 40 to 55% resin acids, and 5 to 10% neutral components) were due to their water-repellent properties rather than their fungicidal properties (Paajanen and Ritschkoff 2002; Alfredson *et al*. 2004; Kartal *et al*. 2006; Panov *et al*. 2010). Timber impregnated with plant oil can serve in aboveground conditions but is not suitable for in-ground contact. Oxidation of impregnated oils takes long time and, meanwhile, part of the oil can be leached (Koski 2008). Thus, immobilisation of plant oil-based wood preservatives and incorporation of organic biocides is an important research direction leading to creosote alternatives.

There is an opportunity to link any plant oil to the wood cell wall and accelerate polymerisation reaction by epoxidizing the oil and subsequently impregnating it in the presence of a catalyst (Treu *et al.* 2004; Temiz *et al.* 2007, 2013). Few publications on the use of epoxidised oils for wood protection were found in the literature. Recently, investigations on the protective properties of ELO have been carried out (Panov *et al*. 2010; Terziev and Panov 2011; Temiz *et al*. 2013), and some promising results were reported. For instance, Terziev and Panov (2011) reported anti-swelling efficiency (ASE) of wood within the range of 50 to 60%, achieved with oil retention of only 80 to 120 kg/m^3. The authors found also a moderate improvement of wood durability in a laboratory decay test performed according to the standard EN 113 (1997). Growth of the fungi *T. versicolor*, *C. puteana*, *P. placenta*, and *G. trabeum* was significantly inhibited. It should also be noted that the wood mass loss was in the range of 10 to 15%, compared to 20 to 30% of the untreated control samples; this is undoubtedly an improvement, but still insufficient if the treated wood is intended for inground use. Even when polymerised, ELO still acts as a nutrient for microorganisms and insects. Temiz *et al*. (2013) carried out an insect test with the larvae of the house longhorn beetle (*Hylotrupes bajulus*), and concluded that ELO (at 200 kg/m^3 retention) benefited the growth of larvae. The survival rate of the larvae was increased in the ELO-treated wood compared to the untreated samples.

In two recent studies (Fernández-Cano 2013; Jebrane *et al.* 2015a,b), Scots pine samples were impregnated with ELO, and the effect of treatment has been studied concerning the Fourier transform infrared (FTIR) spectra, mechanical properties, moisture uptake, and field test performance. The studies confirmed an ASE in the range of 40 to 57%, which was better than the thermally modified (TM) reference samples with only 40% ASE. FTIR analysis of ELO-treated samples revealed that part of the ELO epoxy reactive group was chemically bound to the hydroxyl groups of wood. ELO-treated samples have improved dimensional stability, while the mechanical properties were slightly reduced and the moisture uptake was significantly lowered.

Silicone-based wood formulations are another promising group that relies on achieving hydrophobicity of the treated material. Some products *e.g.,* sodium and potassium silicate preservatives for wood inground contact are already on the market, such as the US company Timber Treatment Technologies markets TimberSIL®, a sodium

silicate wood preservative that ensures a non-toxic, amorphous glass matrix that protects wood fibers. The treated wood is suitable for in-ground exposure, is a fire retardant, and is durable against decay and termite attacks.

A comprehensive review on various investigated and practically applied silicone-based formulations for wood protection was published by Mai and Militz (2004a,b). Alkoxysilanes seem to be efficient, non-toxic, and their by-products are harmless for the treatment facilities. Many alkoxysilanes have been tested, and some methods for their use have been developed (Saka *et al*. 1992; Ogiso and Saka 1993; Bücker *et al*. 2001). The most frequently studied sol-gel process consists of two steps to build up a three dimensional polymer. In a first step the alkoxysilanes are hydrolysed in the presence of an acidic or alkaline catalyst. The obtained solvent (sol) undergoes condensation reaction in the presence of a solvent (gel). After drying of the solvent, a glassy three-dimensional polymer emerges. The advantage of alkoxysilanes in application for wood impregnation is that it can be impregnate into the wood structure and condensate *in situ* due to the small initial size of the oligomers (Saka *et al.* 1992). Alkoxysilanes are also able to enclose additional actives (*e.g*., boron) and limit their leaching (Kartal *et al*. 2009; Panov and Terziev 2009) or enclosing of UV absorbers such as ferric-zirconia-titania (Tshabalala *et al*. 2009) for better durability and weathering performance of wood.

ATR-FTIR and ^{13}C-CP/MAS NMR spectroscopy have confirmed that covalent bond formation occurs between silanes and hydroxyl groups of wood (Mohammed-Ziegler *et al.* 2003; Baur and Easteal 2013). However, remarkable differences of individual silanes have been observed regarding polymerization patterns and reactivity with wood. Silanised wood has anti-swelling efficiency in the range of 30 to 40% and mass loss of 10 to 15% when exposed to basidiomycete fungi (Hill *et al*. 2004; Panov and Terziev 2009). Sebe and Brook (2001) explain the above by the fact that the linkages formed with the cell wall polymer hydroxyl (OH) groups, *e.g.*, Si-O-C bonds, are susceptible to hydrolysis and cannot last long time.

Although studied intensively in laboratory conditions, very little is known about the field performance of alkoxysilanes and modified oils. The objectives of the present study is to show the durability of epoxy-oil modified and alkoxysilane treated wood in a long-term in- and aboveground field testing. Since no visible decay was often revealed, non-destructive mechanical testing of the wood samples during the course of exposure was applied. Considering the results of the literature review, creosote, organic biocides, and boric acid were added to the epoxy-oil and alkoxysilanes, respectively. The intent of the present study was to reveal the five-year field efficacy of these new protective formulations.

EXPERIMENTAL

Materials

Wood

Scots pine sapwood mini-stakes with dimensions of 8 mm × 20 mm × 200 mm along the grain with a standard lap joint were tested according to standard ENV 12037 (1996). Both the inground and aboveground tests used untreated samples as reference. Additionally, thermally modified (TM) Scots pine wood (Thermowood D) was included in the inground test only. The production technology of Thermowood D consisted of treatment in steam at a temperature of 212 °C. Chromium-copper-arsenate (CCA) treated

samples were also included in the reference group as mini-stakes, with 2 and 9 kg/m^3 target retention for the inground test and 4.8 kg/m^3 for the lap-joints. The experiment comprised 30 mini-stakes and 10 lap-joints for each treatment and reference group.

Organofunctional alkoxysilanes, epoxidation, catalyst, and fungicides

Tetraethoxysilane (TEOS), phenyltriethoxysilane (PTES), and methyltriethoxy-silane (MTES), at 98% purity, are commercially available and were purchased from Fluka Analytical (Switzerland). Ethoxysilanes were hydrolysed to silanols using water-ethanol mixtures acidified with 5 mL of 36% hydrochloric acid. Concentrations of solutions were calculated using the mass of initial silanes (not silanols). The molar ratio of boric acid to silane was calculated in all experiments to be 1 to 5. Three concentrations of silanes (23, 16, and 10 wt%) were chosen for impregnation (Table 1). The solution remaining after the first impregnation was weighed and diluted with the calculated amount of water/ethanol mixture to obtain concentrations of 16 and 10 wt%. No more boric acid or other reagents were added.

Table 1. Average Retentions of Alkoxysilane-based Mixtures in Mini Stakes and Lap-joints

	Conc. ratio, ethoxysilane/ boric acid, (%)	Retention in mini stakes, (kg/m^3)		Retention in lap-joints, (kg/m^3)	
		Ethoxysilane	Boric acid (H_3BO_3)	Ethoxysilane	Boric acid (H_3BO_3)
Si(OEt)$_4$	23/1.36	135.2	8.0	–	–
	16/0.95	95.3	5.7	92.0	5.5
	10/0.59	58.8	3.5	62.5	3.7
PhSi(OEt)$_3$	23/1.2	134.6	7.0	–	–
	16/0.83	96.7	5.0	90.1	4.7
	10/0.52	57.5	2.9	62.8	3.3
MeSi(OEt)$_3$	23/1.59	137.4	9.4	–	–
	16/1.1	98.0	6.6	96.3	6.2
	10/0.69	59.0	4.1	58.7	4.0

Linseed oil (LO) and epoxidised linseed oil (ELO) were used throughout the study. The epoxidised linseed oil was prepared according to the method of Chen *et al.* (2002). Hydrogen peroxide was used as an oxidising agent. The iodine value, showing the degree of unsaturation, was determined for the initial and the epoxidised oils; it confirmed the high extent of double-bond conversion. The ELO was mixed with acetic acid as a catalyst.

In order to improve the field performance of the ELO, active ingredients have been added. Creosote type B was mixed with ELO at a ratio of 1 to 3. Retention similar to that recommended by the Nordic Wood Protection Council (NWPC 2014) for hazard class 4 was achieved. Organic biocides were mixed with ELO prior to impregnation; the amount of propiconazole, tebuconazole, and fenpropimorph was in the range of 40 to 130 g/m^3 of treated wood. Benzalkonium chloride (BAC) was added to 1.9 and 0.77 kg/m^3 for wood in-ground and aboveground exposure, respectively (Table 2).

Table 2. Average Retentions (kg/m^3) of ELO-based mixtures in Mini-Stakes and Lap-joints

Samples	ELO	Creosote type B	Benzalkonium chloride (BAC)	Propi-conazole	Tebu-conazole	Fenpropi-morph
Mini-stakes	168					
Mini-stakes	91	31				
Mini-stakes	207		1.9			
Mini-stakes	171			0.051	0.051	
Mini-stakes	217			0.065	0.065	
Mini-stakes	172					0.040
Mini-stakes	192					0.100
Lap-joints	95*					
Lap-joints	96					
Lap-joints	85		0.77			
Lap-joints	93			0.059	0.059	
Lap-joints	139					0.102
* Only reference linseed oil.						

Methods

Impregnation

The alkoxysilanes were impregnated in an autoclave by full-cell method (vacuum 200 mbar for 20 min followed by 8 bar pressure for 90 min). The ELO-mixtures were impregnated by the Rueping process, consisting of pre-pressure (2 to 5 bar) for 30 min, followed by pressure (3 to 8 bar) for 90 min, and final vacuum (500 mbar for 10 min). The target retentions of the studied oils varied from approximately 150 to 220 kg/m^3 for in-ground exposure and from 80 to 140 kg/m^3 for the above-ground test; the alkoxysilanes had retentions in the range of approximately 58 to 138 kg/m^3. All tested alkoxysilanes and ELO combinations and retentions are shown in Tables 1 and 2.

Inground Field Test

The average retentions of the mini-stakes treated with the alkoxysilanes and ELO combinations are shown in Tables 1 and 2. The field in Ultuna (59° 49' N and 17° 40' E) for testing of wood protection formulations and treatments is located in close proximity to the Department of Forest Products at the Swedish University of Agricultural Sciences, Uppsala. The test field provides a clay soil environment with an annual precipitation of 530 mm. The prevailing types of decay are soft rot and bacteria, which yield a service life of 2 to 3 years (Edlund 1998) for standard stakes of untreated Scots pine sapwood, according to EN 252 (1989). The water holding capacity of the soil from the Ultuna test field is approximately 50% (w/w) (Edlund 1998).

Modulus of Elasticity (MOE) Measurements of Inground Exposed Wood

The mini-stakes exposed in the ground were analysed to reveal changes in MOE. For determination of MOE, a universal testing machine (Shimadzu AG-X 50 KN; Japan) was used. The MOE was measured according to the ISO 3349 (1975) standard under the recommendations suggested by Stephan *et al.* (1996). The measurements were carried out after 4, 12, 18, 24, 30, and 42 months of exposure. The difference between the MOE of the mini-stakes prior to the exposure in the test field and after defined exposure intervals was calculated as a percentage of the initial modulus.

Aboveground Field Test

The aboveground field test was carried out according to the standard ENV 12037 (1996). The average retentions of the lap-joints treated with the alkoxysilanes and ELO combinations are shown in Table 1 and 2. The lap-joints were conditioned for one month to an approximate moisture content of 12%. The test started in March 2007, and is ongoing. All lap-joints have been weighed monthly. The results shown comprise 62 months of exposure.

RESULTS AND DISCUSSION

Inground test

The intent of the study was to provide valuable information on the field performance of two groups of formulations, namely alkoxysilanes and ELO combinations. The former are subject to hydrolysis as soon as exposed outdoor, while the later still provide nutrients for the microorganisms which justified the addition of biocides. The biocides were applied at retentions that were lower than the respective minimum effective concentrations.

The decrease of MOE for the reference mini-stakes is illustrated in Fig. 1. Samples that have lost more than 75% of the initial MOE are considered broken and removed from the test. The average MOE of the untreated mini-stakes reached this value after 34 months of exposure, a result that is similar to the average service life of untreated stakes (according to standard EN 252 1989) exposed in the same field. The TM samples showed a 47% reduction of MOE, attesting that TM wood is not suitable for inground use. Loss of MOE of the TM stakes is proven to be accentuated by extensive micro-checking produced in the TM wood tracheids during the original heat treatment and consequent biological attack of soft rot and bacteria (Råberg *et al.* 2012). The smallest reduction of MOE was demonstrated by CCA-impregnated stakes being 21% and 8% for the lower and higher concentrations, respectively.
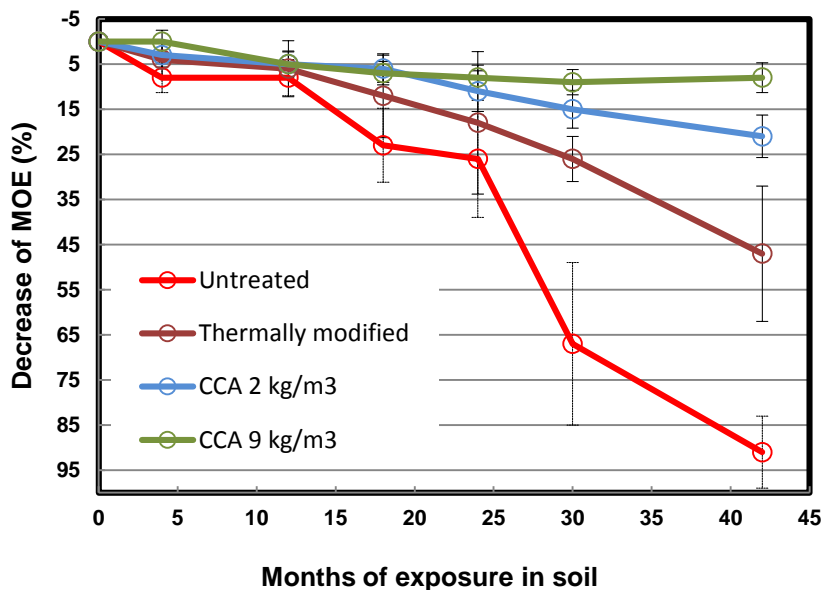

Fig. 1. Decrease of MOE for the reference samples after 42 months of exposure in ground contact. The vertical bars represent standard deviations

The loss of MOE for alkoxysilane-treated mini-stakes is shown in Fig. 2. For simplification of the figure, the standard deviations are not shown. The pattern of MOE loss for this group of samples attests that the studied alkoxysilanes have no potential as preservatives for wood in ground contact. Particularly poor performance is demonstrated by TEOS-treated mini-stakes, which despite the test concentration, failed after 25 to 35 months, behaving like the untreated samples. The PTES and MTES showed MOE loss in the range of 15% to 22%, similar to that of the CCA-treated ($2 \ kg/m^3$) stakes (Fig. 1); the expected service life of these stakes is approximately 6 years. The MOE loss of both PTES and MTES samples did not show response to the applied concentration.
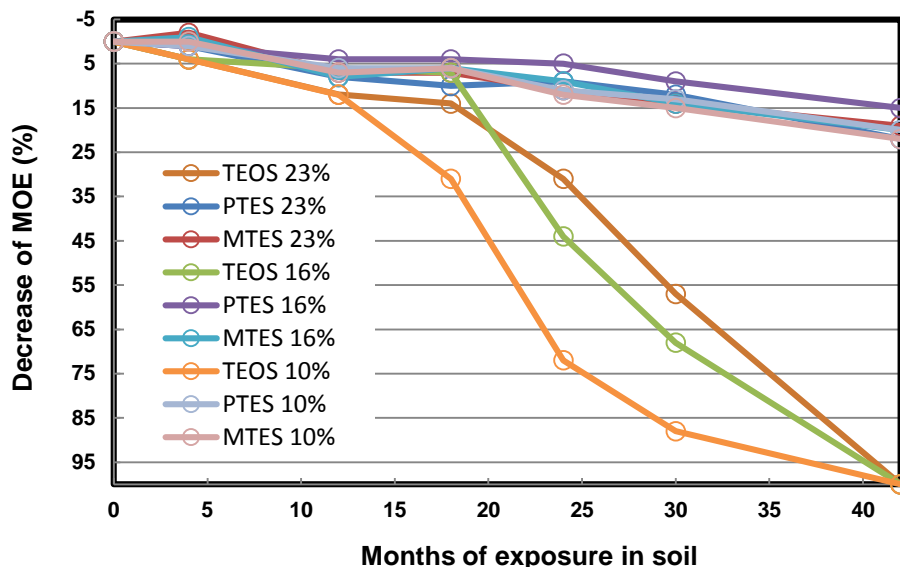

Fig. 2. Decrease of MOE for the alkoxysilane- and H_3BO_3-treated samples after 42 months of exposure in ground contact

The solutions of alkoxysilanes can easily be impregnated in the wood cell wall (Terziev *et al.* 2009) but the eventual effect of the chemical or/and electrostatic bonding between the alkoxysilanes and wood hydroxyl groups is difficult to trace because such bonding can be hydrolysed and the products (low-molecular fractions) leached. This seems to be more valid for TEOS-treated mini-stakes. The results contradict the laboratory findings of Panov and Terziev (2009), in which the addition of boric acid to silanols resulted in highly improved durability of wood, *i.e.* mass loss of 1.1 to 2.3%. Long-term exposure in ground contact is able to hydrolyse and leach the tested alkoxysilanes and boric acid in the TEOS-treated mini-stakes while PTES and MTES are more stable and, probably, more difficult to hydrolyse.

The loss of MOE for ELO-treated mini-stakes is shown in Fig. 3. Mini-stakes treated only with ELO at 168 kg/m^3 behaved similarly to the TM stakes, showing 43% loss of MOE. Addition of any biocide improved the performance of the material. For example, benzalkonium chloride, fenpropimorph, and propiconazole and tebuconazole at 1900, 100, and 65 g/m^3, respectively, were enough to boost the performance of mini-stakes treated with ELO to a level similar to that of CCA-treated ($9 \ kg/m^3$) stakes. A positive result was also achieved when ELO was used alongside creosote present at 30 kg/m^3; the loss of MOE after 42 months of exposure was only 8%.
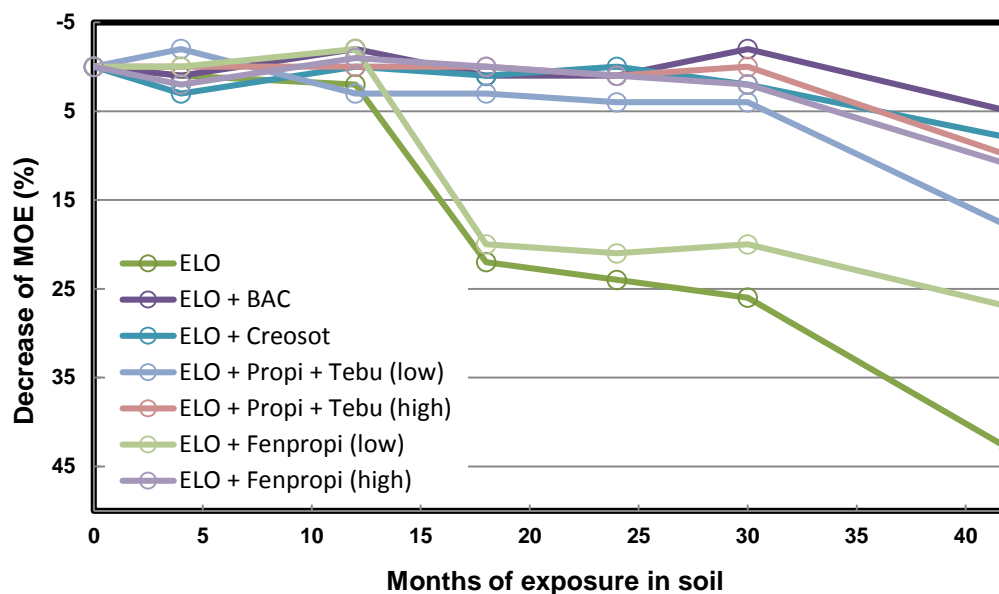
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Fig. 3. Decrease of MOE for the ELO- and fungicide-treated mini-stakes after 42 months of exposure in ground contact

Scots pine samples impregnated with ELO showed the effect of the treatment on the induced chemical changes (Jebrane *et al.* 2015b). FTIR analysis of ELO-treated samples revealed that part of the ELO epoxy reactive group was chemically bound to the wood hydroxyl groups, *i.e.* the wood is modified by means of ELO. Apparently, this is not enough to prevent decay in ground contact, even when 40 g fenpropimorph is added to the ELO. At higher retention, the organic biocides are effective due to their immobilization by the polymerized oil which hinders their leaching. The mixture of ELO and creosote is an example of a step towards a less harmful alternative to creosote.

Aboveground test

The aboveground performance of alkoxysilane-treated lap-joints after 5 years of exposure is shown in Figs. 4. The dynamics of moisture content (MC) of lap-joints exposed for 60 months revealed that PTES and MTES are very efficient in keeping the wood MC below 35% during the whole year (Fig. 4). Tetraethoxysilane (TEOS) was not effective; the TEOS-treated lap-joints behaved like the untreated samples and thus, some similarity to the inground test can be traced. The water uptake of PTES and MTES-treated wood was considerably diminished, due to the high water repellence of these two alkoxysilanes. This observation is similar to that of Donath *et al.* (2006, 2007) who also found MTES to be suitable for aboveground use.

The ELO-treated lap-joints demonstrated somewhat better hydrophobic properties than that treated with alkoxysilanes (Fig. 5). Moisture content of the lap-joints treated with ELO was lower and always below 25%. The reference lap-joints treated only with LO had double the MC of the ELO-treated samples. The aboveground test with alkoxysilanes, LO, and ELO was valid because the untreated lap-joints showed a median decay rank of 3.5, *i.e.*, half of the samples were heavily decayed, while the second half was completely failed (according to ENV 12037, 1996). The lap-joints treated with TEOS had a median decay rank of 2.0. No decay was observed on samples treated with CCA, PTES, MTES, LO, or ELO, alone or in combination with the tested biocides. The PTES and MTES were found

to be very effective in aboveground exposure at 60 kg/m^3 of silanes with the addition of 3 to 4 kg/m^3 of boric acid.
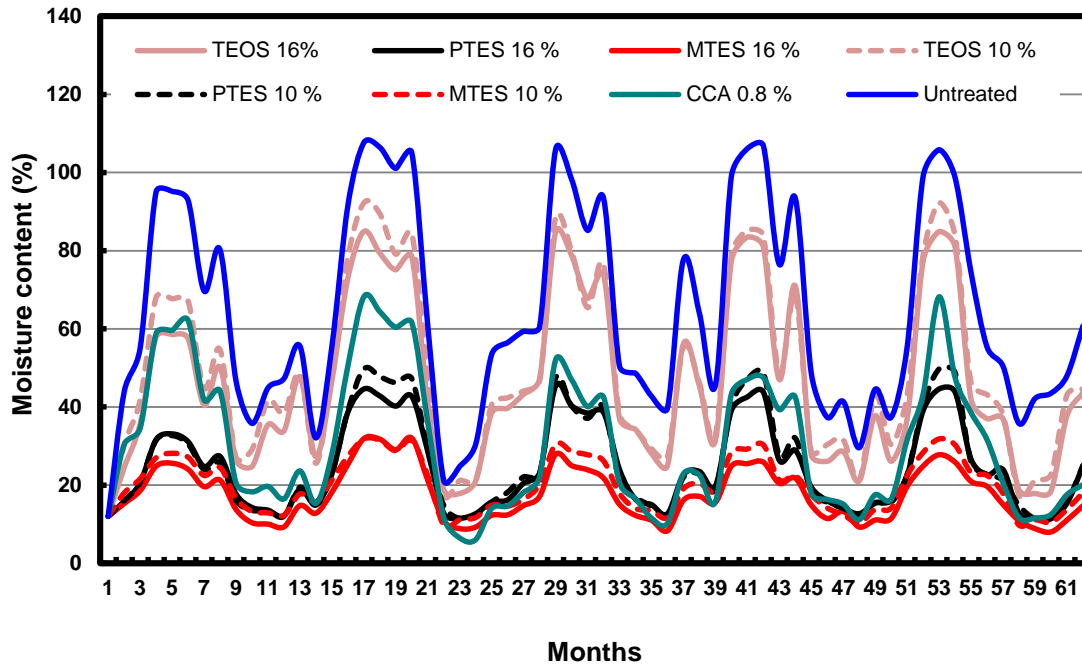

Fig. 4. Moisture content dynamics of reference and alkoxysilane-treated lap-joints with the addition of H_3BO_3 during 62-month exposure in the Ultuna field
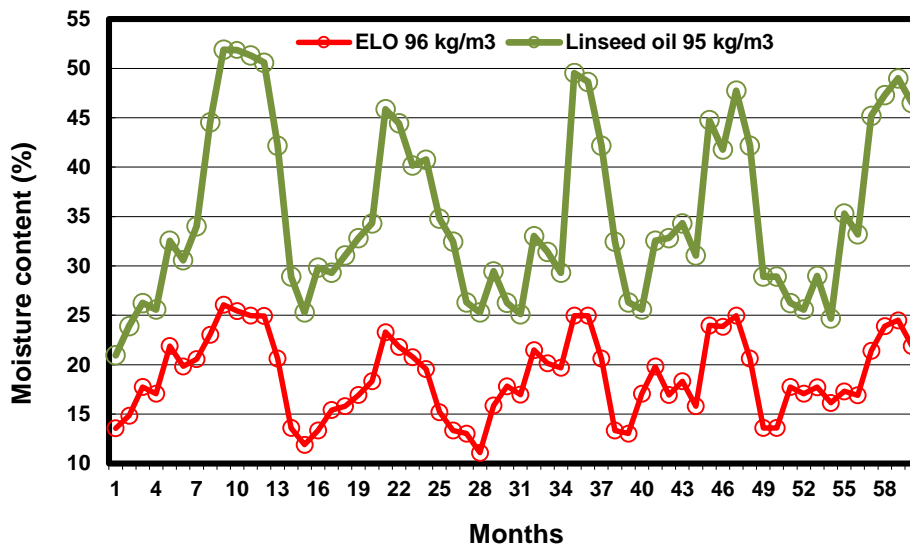

Fig. 5. Moisture content dynamics of only LO-treated and ELO-treated lap-joints without biocides during 60-month exposure in the Ultuna field

The studied organofunctional alkoxysilanes and ELO introduced hydrophobic properties to wood, while durability measured by the laboratory test EN 113 (1997) was improved only marginally; this effect has been evidenced in previous studies (Panov and Terziev 2009; Terziev and Panov 2011). The above results suggest addition of biocides to further improve wood durability. On the other hand, De Vetter *et al.* (2009) found that the

combination of organosilanes and biocides neither change the protective effectiveness of the treated wood nor reduce the toxicity of their leachates either. However, the authors have tested other alkoxysilanes and only in laboratory conditions. In the present study, the applied amount of the biocides BAC, propiconazole, tebuconazole, and fenpropimorph showed an effective synergy with ELO, and the loss of MOE in the ground contact test was similar to that of CCA-treated samples at 9 kg/m^3 retention.

Particularly interesting is the finding that the amount of creosote can be reduced to 25% of the recommended retention; the rest can be substituted by ELO. This finding opens new possibilities for further research aimed at combining biocides with epoxidised oils to create hydrophobic agents that also prevent leaching of chemicals. The ELO is more effective than LO alone when the treated timber is intended for aboveground exposure; in this case, there is no need for additional biocides because five-year aboveground exposure revealed identical durability of CCA- and ELO-treated lap-joints.

CONCLUSIONS

1. The studied alkoxysilanes (TEOS, PTES, and MTES) have no potential as preservatives for inground contact, despite the applied concentrations and added boric acid. The expected service life of the treated wood is approximately six years.

2. PTES and MTES are efficient hydrophobic agents for wood in aboveground exposure, keeping always the wood moisture content below 35%. The effective retention was 60 kg/m^3 of silanes with addition of 3 to 4 kg/m^3 of boric acid.

3. Addition of biocides (BAC, propiconazole, tebuconazole, and fenpropimorph) to ELO improved the performance of material in ground contact to a level similar to that of CCA-treated stakes (9 kg/m^3).

4. The amount of creosote can be reduced to 25% of the retention recommended by the Nordic Wood Protection Council for hazard class 4; the rest can be substituted by ELO. This does not influence the efficacy of the formulation.

5. The moisture content of wood treated with ELO and exposed aboveground (lap-joints) was lower than that of the wood treated with PTES and MTES and always below 25%.

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