Field performance of epoxi-oil modified and alkoxysilane treated wood

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Keywords: above-ground exposure, creosote, epoxidised linseed oil, fenpropimorph, propiconazole, alkoxysilanes, tebuconazole

ABSTRACT

Increased interest to oils and silicones as hydrophobic agents urges testing of their field performance for better understanding and preparation for an eventual market entrance of these products. The study reveals above ground field test performance of wood impregnated with epoxidised linseed oil (ELO) and organofunctional alkoxysilanes as well as compares the achieved results with significantly more severe in-ground 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 were impregnated and tested alone or in combination with boric acid, organic fungicides and creosote. Untreated, CCA treated and thermally modified samples served as references. Long term above and in-ground testing of the studied formulations enforces the conclusion that ELO and alkoxysilanes are suitable formulations for timber exposed above ground. No decay was registered in the two groups of treated lap joint samples while the untreated controls were close to failure after 5 years of exposure. Another outcome of the study was the confirmation that a standard laboratory decay test is not designed to predict the above ground performance of modified wood. Time will show whether the above ground test will demonstrate similar proportions of decay and failure between the treated and untreated samples as wood exposed in-ground.

INTRODUCTION

Wood protection has passed through a significant metamorphosis - from using of highly toxic formulation containing arsenate at high retentions to entirely copper- and organic-based preservatives and introduction of modified wood on the market in the recent decades. Arsenate has gone to the protection history, chromium and boron compounds are still in use but under hard debates regarding the environment and health consequences for their further use. Creosote is also a wood preservative that can be banned soon. Known for more than 200 years, creosote has still restricted but irreplaceable role in protection of wooden poles and railway sleepers. The price of creosote has been doubled in the recent decade. In some countries, *e.g.* Sweden, an additional tax on creosote might be introduced soon. In Europe the use of creosote is permitted until 2018; its further use is debatable.

The written above offers a good reason for research pointed at development of formulations and methods that can eventually substitute the creosote as well as alternative protection for wood in ground contact. The existing and allowed alternatives are not many 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*. bandages and boots in soil contact 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 protection of wood in- and above ground exposure. Based on a great number of investigations revealed the possible use of plant oils as a means of wood protection, a general conclusion is drawn that the main effect of plant and tall oils lies in the water repellency rather than in the oil's fungicidal properties (Panov *et al.* 2010, Paajanen and Ritschkoff 2002, Kartal *et al.* 2006, Alfredson *et al.* 2004). Another alternative is the use of sodium and potassium silicate-based preservatives for wood in ground contact. For instance, the US company TTT markets TimberSIL®, a sodium silicate wood preservative that ensures a non-toxic, amorphous glass matrix of the substrate. The treated wood is suitable for in-ground exposure, it is fire-retardant and durable against decay and termite attacks.
Alkoxysilanes seem to be a promising group of compounds that are not toxic and their by-products are harmless for wood and treatment facilities. A long list of alkoxysilanes has been tested and some methods for their use have been developed (Saka *et al*. 1992, Ogiso and Saka 1993, Bücker *et al*. 2001). In contrast to alkoxylanes, only few publications on the use of epoxidised oils for wood protection were found in the literature. Recent investigations on 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 50-60 %, with oil retentions of only 80 to 120 kg/m^3. The authors also found a moderate improvement of wood durability in a laboratory decay test performed according to EN 113 (1997). The 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 10-15 % compared to 20-30 % of the untreated control samples - undoubtedly improvement but far not enough if the treated wood is intended for in-ground use. Even when polymerised, ELO can still act as a nutrient for microorganisms and insects. Temiz *et al.* (2013) carried out an insect test with 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 untreated wood.
At the time of writing this manuscript, alkoxysilane and ELO treated Scots pine (*Pinus sylvestris*) sapwood samples are still under evaluation in above and in-ground field test in Uppsala, Sweden. Some preliminary results after 30 months exposure have already been presented (Terziev and Panov 2011) only for lap-joints treated with LO and ELO (at retentions of 96 and 76 kg/m^3 respectively). The intent of the present study was to reveal the 5-year field efficacy of these protective methods.

MATERIAL AND METHODS

Wood material

Scots pine sapwood mini-stakes with dimensions 8×20×200 mm along the grain as well as standard lap-joint (according to standard ENV 12037) samples were used in the tests. Both in- and above ground tests used untreated samples as reference. Additionally, thermally modified (TM) Scots pine wood (Thermowood D) was included only in the in-ground test. The production technology of Thermowood D consisted of a 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 retention for the in-ground test and 4.8 kg/m^3 retention 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), methyltriethoxysilane (MTES) are commercially available and were purchased from Fluka (98% purity). Hydrolysed alkoxysilane was mixed with boric acid (H_3BO_3). The amount of boric acid was calculated considering 5 mol of alkoxysilane to one of boric acid. Three concentrations containing the respective silane and H_3BO_3 at 23 and 1.3%, 16 and 1.12%, 10 and 1.58% were tested in- and above ground exposure.

Linseed (LO) and epoxidised linseed oil (ELO) were used throughout the study. ELO was prepared according to Chen *et al.* (2002). Hydrogen peroxide was used as oxidising agent. Iodine values as degree of unsaturation were determined for initial and epoxidised oils. ELO was mixed with acetic acid as catalyst.

Creosote type B was used in the study. Retention similar to the recommended one for hazard class 4 was prepared. Creosote was mixed with ELO at an approximate ratio 1:3.

All biocides were mixed with ELO prior to impregnation; the amount of propi-, tebuconazole and fenpropimorph was in the range of 40-130 g/m^3 while benzalkonium chloride (BAC) was added as 1.9 and 0.77 kg/m^3 for wood in- and above ground respectively (Table 1). The mass of remaining mixture was always determined after impregnation and additional quantities of the test biocide were calculated.

Impregnation

The alkoxysilanes and oils were impregnated in an autoclave using pressure and vacuum. The retentions of the studied oils varied from approximately from 80 to 200 kg/m^3; the alkoxysilanes had retentions in the range 60-140 kg/m^3. All tested ELO combinations and retentions are shown in Table 1.

In-ground field test

Ultuna test field (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 SLU, Uppsala. The test field provides a clay soil environment with an annual precipitation of 530 mm. The prevailing type of decay is soft rot and bacteria which provides a service life of 2 to 3 years (Edlund 1998**)** for standard stakes of untreated Scots pine according to EN 252 (1989). The water holding capacity of the soil from the Ultuna test field is approximately50% (m/m) (Edlund 1998).

Modulus of elasticity measurements of in-ground exposed wood

The mini-stakes exposed in-ground were analyzed to reveal changes in MOE. For determination of MOE, a universal testing machine (Shimadzu AG-X 50 KN) was used. The MOE was measured according to the ISO 3349 standard under the recommendations suggested by Stephan *et al.* (2001). 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.

Above ground field test

The above ground field test is carried out according to standard ENV 12037 (2002). The average retentions (76-136 kg/m^3) of the LO, ELO and added biocides are shown in Table 1. The lap-joints were conditioned for a month and then weighed together with the plastic bands to represent a weight at approximately 12% moisture content. All lap-joints are weighed monthly. The test started in March 2007 and is still on-going. The results shown comprise the first 5 years of exposure.

RESULTS

All tested ELO combinations are shown in Table 1.

Table 1: Description of the ELO tested formulations. All retentions are expressed as average in kg/m^3

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	96[a]					
Lap-joints	76					
Lap-joints	85		0.770			
Lap-joints	93			0.059	0.059	
Lap-joints	139					0.102

[a]*Only linseed oil*

The retention of ELO treated mini-stakes varied between 91 to 217 kg/m^3. All biocides were applied at retentions that are significantly lower than the respective minimum effective concentrations. The decrease of MOE only for the reference mini-stakes is demonstrated in Figure 1. Samples that have lost more than 75% of the initial MOE can

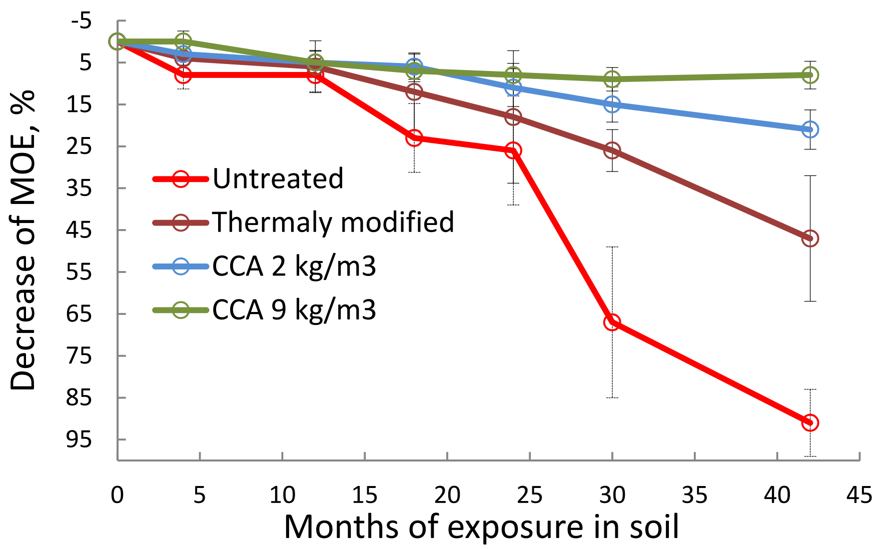

Figure 1: Decrease of MOE for the reference samples after 42 months of exposure in ground contact. The vertical bars represent standard deviations.

be considered broken, *i.e.* out of 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 (EN 252) exposed in the field. TM samples showed 47% reduction of MOE thus proving that TM wood is not suitable for in-ground exploitation. The lowest reduction of MOE was demonstrated by CCA impregnated stakes reaching 21 and 8% along with the increase of concentration.

The loss of MOE for alkoxysilane treated mini-stakes is shown in Figure 2. For simplification of the Figure, the standard deviations are not shown.

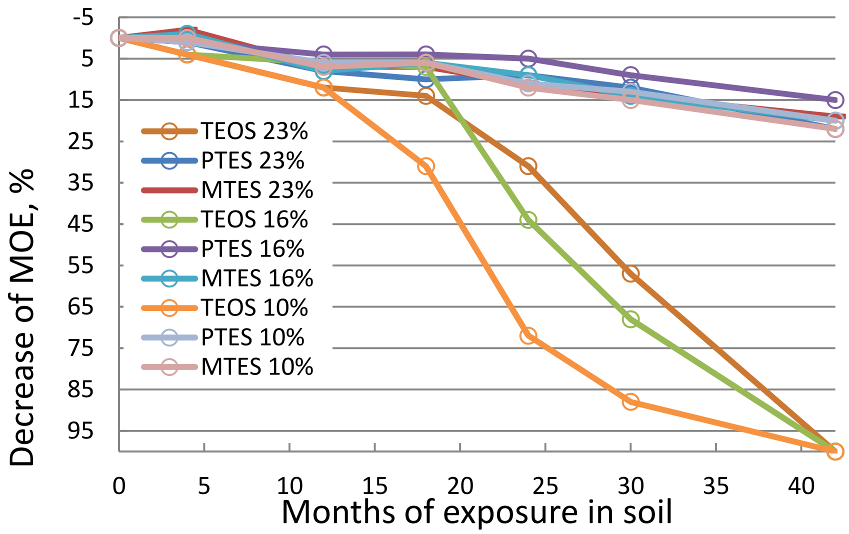

Figure 2: Decrease of MOE for the alkoxysilane and H_3BO_3 treated samples after 42 months of exposure in ground contact.

The pattern of MOE loss for this group of samples proves that the studied alkoxysilanes have no potential as preservatives in ground contact. Particularly poor performance is demonstrated by TEOS treated mini-stakes that, despite the test concentration, went to failure after 25-35 months, *i.e.* behaved as untreated samples. PTES and MTES showed MOE loss in the range of 15 to 22%, *i.e.* similar to that of the CCA (2 kg/m^3) treated stakes (Figure 1) and thus the expected service life of these stakes is approx. 6 years. The MOE loss of both PTES and MTES samples did not show response to the applied concentration. The loss of MOE for ELO treated mini-stakes is shown in Figure 3.

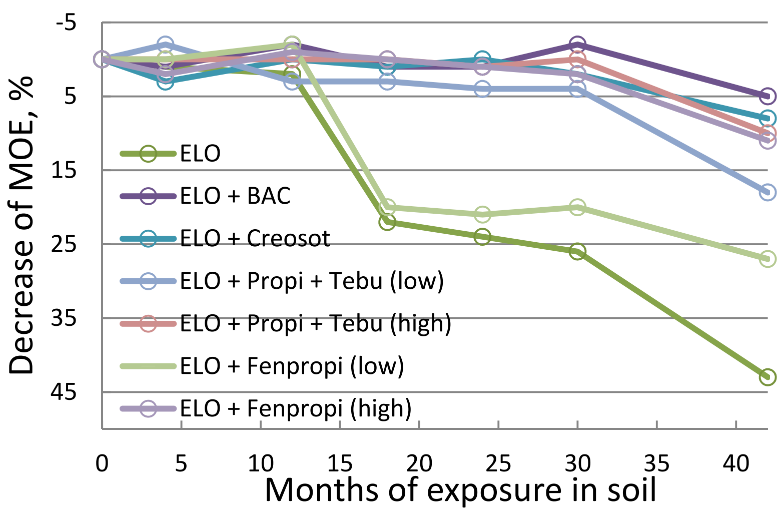

Figure 3: Decrease of MOE for the ELO and fungicide treated mini-stakes after 42 months of exposure in ground contact.

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 significantly the performance of material. For example, benzalkonium chloride, fenpropimorph, probi- and tebuconazole at 1900, 100 and 65 g/m^3 are enough to boost the performance of stake treated with ELO to a level similar to that of CCA treated stakes (9 kg/m^3). A positive result is achieved when ELO is mixed with only 30 kg/m^3 creosote; the loss of MOE after 42 months of exposure is only 8%.

The above ground performance of alkoxysilane, LO and ELO treated lap-joints after 5 years of exposure is shown in Fig. 4 and 5. Dynamic of moisture content (MC) of lap joints exposed for 60 months revealed that phenyl- and metyltriethoxysilane (PTES and MTES) are efficient hydrophobisators, thus keeping the wood MC below 35% during the whole year while tetraethoxysilane (TEOS) was not effective and behaved likely the untreated samples. ELO treated wood demonstrated somewhat better hydrophobic properties than that treated with alkoxysilanes. The moisture content of lap joints treated with ELO was lower and always below 25%. The reference lap joints treated with only LO has double as high MC as the ELO treated samples. The above ground test with alkoxysilanes, LO and ELO was valid since the untreated lap joints showed a median decay rank of 3.5, *i.e.* half of the samples were heavily decayed; the second half was gone to failure. The lap joints treated with TEOS had a median decay rank of 2.0. No decay was observed on samples treated with CCA reference joints, PTES, MTES, LO and ELO treated lap joints - alone or in combination with the biocides.

DISCUSSION AND CONCLUSIONS

The studied organofunctional alkoxysilanes and ELO introduce hydrophobic properties to wood while durability measured by a laboratory test was improved only marginally. This is proved in previous studies, e.g. Panov and Terziev (2009) and Terziev and Panov (2011). The above implied the addition of biocides to improve further the wood durability.

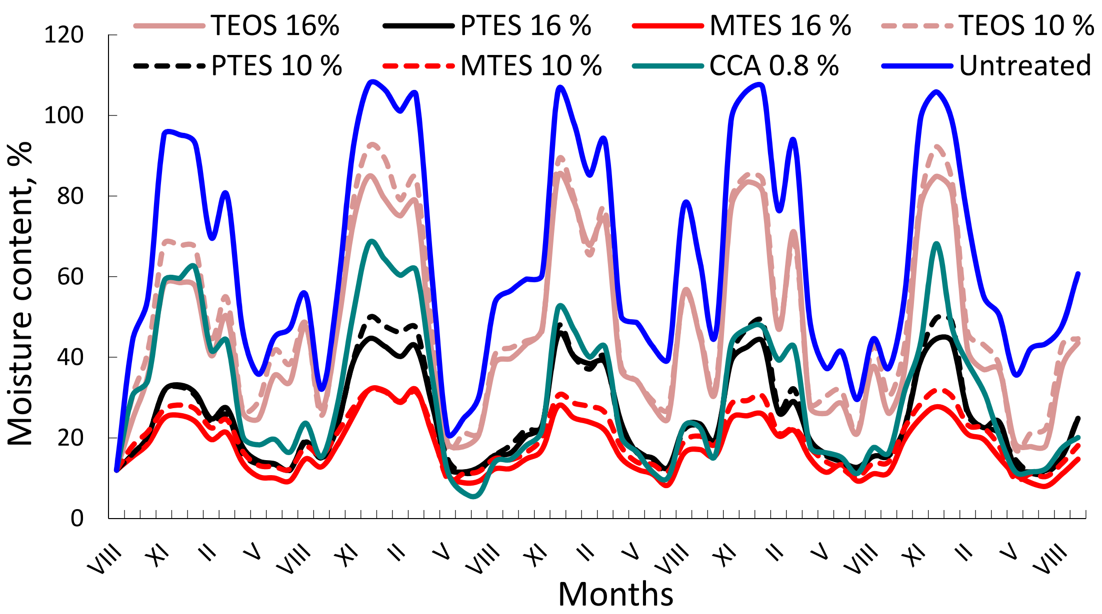

Figure 4: Moisture content dynamics of reference and alkoxysilane treated lap-joints with addition of H_3BO_3 during 5-year exposure in the field of Ultuna.

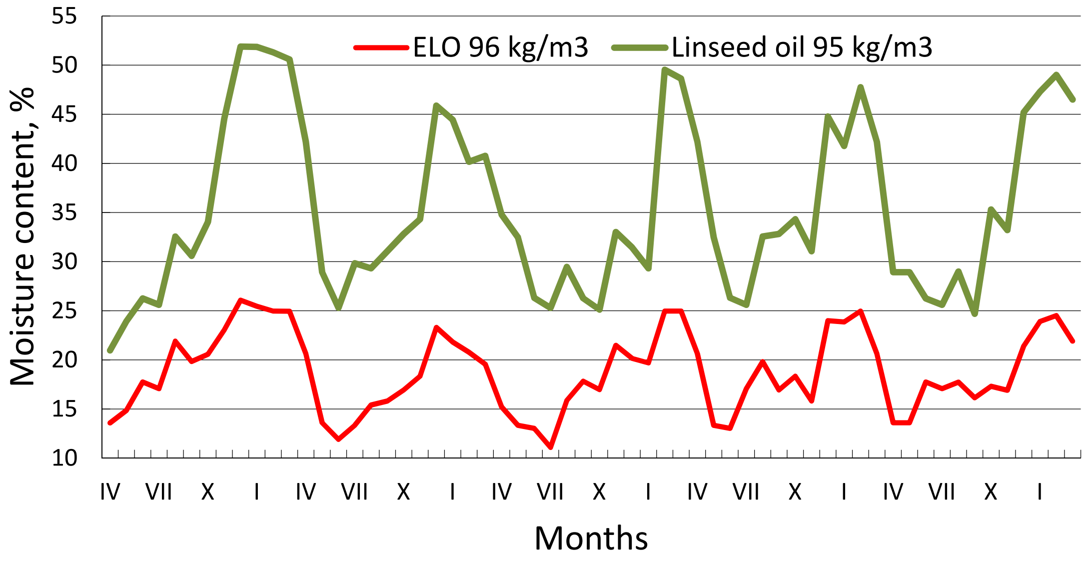

Figure 5: Moisture content dynamics of reference, LO and ELO treated lap-joints without biocides during 5-year exposure in the field of Ultuna.

The applied amount of biocides, *i.e*. BAC, propi-, tebuconazole and fenpropimorph, showed an effective synergy with ELO and the loss of MOE in ground contact test was similar to that of 9 kg/m^3 retention of CCA treated samples. 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 possibility for further research aimed at combining biocides with epoxidised oils as hydrophobic agents preventing leaching of chemicals. The ELO is significantly more effective than only LO when the treated timber is aimed for above ground exposure; in this case there is no need of additional biocides since 5-year above ground exposure revealed identical durability of CCA and ELO treated lap joints. The studied alkoxysilanes had no efficacy when the treated wood was exposed in ground contact. However, PTES and MTES were found to be very effective in above ground exposure at 10% concentration and addition of 1.58% H_3BO_3.

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