

Drying of linseed oil wood coatings using reactive diluents

C Stenberg,¹ M Svensson,² E Wallström³
and M Johansson¹

1 The Royal Institute of Technology, Fibre & Polymer Technology,
KTH, SE-100 44 Stockholm, Sweden

2 Svenska Lantmännen, Box 30192, 104 25 Stockholm,

3 EnPro ApS, Lersø Parkallé 42, DK-2100 København Ö, Denmark

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Summaries

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Studies of the drying of two linseed oils with different fatty acid patterns, oil A (74.2% linoleic acid) and oil B (55.2% of linolenic acid), show that the structural variations and the addition of the methyl ester of oil A as a reactive diluent (0, 20 and 40wt%) influenced the drying performance and final film properties of the oils.

The incorporation of reactive diluents reduced the effects of surface sealing for oil B at higher temperatures and increased the through-drying rate of oil B. Softer coatings were obtained for both oils when using a reactive diluent. Chemical reactions induced by the wood substrates are shown to affect the drying.

For correspondence contact

M Johansson

The Royal Institute of Technology, Fibre & Polymer Technology,
KTH, SE-100 44 Stockholm, Sweden

Tel: +46 8 790 92 87

Email: matskg@polymer.kth.se

Fax: +46 8 790 89 34

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Introduction

Linseed oil is a renewable natural resource, containing high proportions of unsaturated linoleic and linolenic acids. Linseed oil is a drying oil which dries slowly upon exposure to air, forming a coating by a complex auto-oxidative cross-linking mechanism that is still not completely understood.¹

Linseed oil has a long tradition of being used in paints, varnishes, and in modified alkyd resins.² It is superior as a wood protection product because of its hydrophobic properties, and its ability to penetrate and impregnate wood upon drying, giving good protection against moisture and water diffusion. Other factors affecting the penetration into wood are the viscosity of the oil, and the chemical reactivity between oil and wood.³

Disadvantages in wood protection, such as problems with yellowing, poor long-term stability, rather soft films, and the slow drying rate, are reasons for the replacement of linseed oil by synthetic coatings such as alkyds and latex coatings.

Improved knowledge including modern crop development and production techniques has made it possible to design the linseed oil structure.⁴⁻⁶ This has resulted in linseed varieties with higher yields, increased content of unsaturated fatty acids (higher iodine values), and controlled oil content.⁷⁻⁹ By removing as much as possible of the unpalatable and easily oxidised linolenic acid, the risk for unpleasant rancidity problems with products is decreased. However, this also leads to fewer carbon-carbon double bonds shown by a decreased iodine value. By tradition, this has made the oil to be regarded as unsuitable in paint and coating applications.

Because of the rather slow oxidation rates, the oil is often pre-polymerised.² There are several methods to pre-polymerise linseed oil (eg boiled oil, stand oil and blown oil). These methods increase the viscosity of the oil, which makes it more difficult to apply, and lowers its ability to penetrate into the wood without the use of an organic solvent to lower the viscosity. The need to avoid volatile organic compounds (VOCs) as solvents in paints has been forcing the development of environment-friendly paints.¹⁰ Changing the solvent to use water-based paints (eg water-borne alkyds) is one solution, but it is not free from problems such as longer drying times compared with solvent-based paints.¹¹ The use of reactive diluents is

another way to avoid solvents. A reactive diluent lowers the initial viscosity during paint application. Upon drying it becomes part of the polymer matrix. Reactive diluents must be soluble in the undried media and have a good reactivity to remain chemically bonded in the final film.¹²

The substrate influence on the drying is of importance. Physical properties of the wood substrate, such as moisture content, age, type of wood, the direction of the wood fibres on the substrate, and chemical substances in the wood such as lignin, could affect the oxidative drying of the impregnating oil.

The first part of this paper presents a study on how a reactive diluent based on the methyl ester of oil A, containing mainly methyl linoleate, is affecting the drying of two different linseed oils. The second part describes how a pinewood substrate influences the oxidative drying of the linseed oils. Real-time infrared (RTIR) spectroscopy and chemiluminescence (CL) were chosen as analytical techniques.

Experimental

Materials

Oil coating formulations

Oils from two different varieties of linseed (*Linum usitatissimum*) were prepared, analysed and supplied by Svenska Lantmännen (Sweden). Oil A (Purolin[®]) originated from an edible vari-

ety of linseed and had a large content of linoleic acid (C18:2). Oil B originated from a traditional variety of linseed and had a large content of linolenic acid (C18:3). All chemicals were used without further purification.

Oil A (Purolin) and the reactive diluent (Linutin[®]) was obtained from Svenska Lantmännen (Stockholm, Sweden). Oil B (refined linseed oil) was obtained from Solutia Denmark A/S (Søborg, Denmark). The oil formulations were mixed at Enpro ApS (Copenhagen, Denmark).

The composition of the oil formulations is presented in Table 1. Furthermore, two references containing the pure oils A and B without driers and reactive diluents were chosen for the experimental studies. The methyl ester of oil A (Linutin) was used as a reactive diluent. The fatty acid patterns of the reactive diluent and the two different oils are presented in Table 2.

The driers

A commercial mixture of a primary drier, Co-10 HEX-CEM (10wt% Cobalt) from OMG Europe (Dusseldorf, Germany), a through-drier Z-18 HEX-CEM with 18wt% of Zr metal (OMG, Germany), and an auxiliary drier Octa-Soligen Calcium 10 (Borchers GmbH, Langenfeld, Germany) with 10wt% of Ca were used. When the drier mixture was added to the oil blends, the metal content was 0.0024wt% Co-metal, 0.0034wt% Zr-metal, and 0.0040wt% Ca-metal (ie a total metal content of 0.01wt%).

Table 1: The composition of the evaluated formulations

Sample	Oil content (RD = reactive diluent)	Drier total wt % metal (Co:Zr:Ca)	Viscosity (mPas)
1	100% oil A	0.01%	69.0
2	80% oil A and 20% RD	0.01%	39.6
3	60% oil A and 40% RD	0.01%	26.6
4	100% oil B	0.01%	59.0
5	80% oil B and 20% RD	0.01%	40.8
6	60% oil B and 40% RD	0.01%	25.2
7	40% oil A, 40% oil B and 20% RD	0.01%	41.0
8	100% oil A	No drier	–
9	100% oil B	No drier	–
10	0 % (100% pine heartwood lath)	–	–

Table 2: The fatty acid composition (%) of the linseed oils A and B. The oils mainly differ in the content of the reactive fatty acids (ie linoleic (C18:2) and linolenic (C18:3) acid)

Fatty acid	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	>C20:0
Oil A	6.0	0.1	3.3	13.0	74.2	2.7	0.5
Oil B	5.0		3.3	19.3	14.6	55.2	2.6
Reactive diluent methyl ester of oil A	6.0	0.1	3.3	13.0	74.2	2.7	0.5

The substrates

In the real-time infrared spectroscopy (RTIR) measurements, oil droplets were all applied on the attenuated total reflectance (ATR)-crystal device. For the chemiluminescence (CL) measurements, two different substrates were used. Aluminium pans (diameter 20mm) and Swedish pine heartwood lath plates were supplied by Växjö Universitet, Växjö, Sweden. Pinewood plates measuring 200 × 100 × 8mm (longitudinal, radial, tangential directions) were cut out with a saw into plates with a size of 20 × 20 × 8mm (longitudinal, radial, tangential directions). The small wooden plates were finally split in two halves (20 × 20 × 4mm) in order to fit in the CL apparatus. The oils were applied on the split side, at 45° to the radial direction, on the wood substrates. The oil formulations are denoted with 1a to 9a corresponding to aluminium, or 1b to 9b corresponding to wood as the substrate when presenting the results of the CL measurements.

Instruments and procedures

Chemiluminescence (CL) measurements

Chemiluminescence measurements were performed on an apparatus built by Färnert Digitalteknik (Stockholm, Sweden). Emitted photons were detected with a Hamamatsu H6180-01 integrated photon counting head. The oil sample (20mg) was applied by weighing directly on an aluminium test plate or applied on top of wood substrates, and then placed in a temperature- and air-flow-controlled test chamber inside the CL apparatus. Before inserting the samples, the desired temperature (70°C) in the test chamber was well established. As soon as a vacuum was received around the test chamber, the counting of emitted photons was started. Data were collected once every minute. The atmosphere in the chamber was controlled by a constant airflow, 60ml/min, during the whole experiment. This made it possible to run comparable experiments in both the RTIR and the CL, following the auto-oxidation reactions in real time.

Real-time infrared spectroscopy (RTIR) measurements

Infrared spectra were recorded on a Perkin Elmer Spectrum 2000 FTIR equipped with a heat-controlled single reflection ATR accessory (Golden Gate) from Specac Ltd (Kent, England). The heat controller was set to the desired temperature of 70°C. When the temper-

ature was established on the ATR accessory, the oil sample (approximately 5µl of oil) was applied onto the ATR-crystal, leaving an oily thin film. The infrared (IR) measurements were commenced directly after the oil was applied, and spectra were recorded using Timebase® software from Perkin-Elmer every ten minutes. The total length of each measurement was set to 30 hours (1800 minutes), resulting in a total of 180 spectra (16 scans per spectrum, resolution of 4cm⁻¹). The surrounding atmosphere was air.

Hardness of dry film (pendulum hardness)

Pendulum hardness measurements were performed according to ISO 1522-73, 'Pendulum damping test', after different periods of drying time. The samples were all applied and dried on glass plates. The wet film thickness was 60µm. All measurements were made in a controlled climate room at a temperature of 23 ± 2°C and at a relative humidity of 50 ± 5% during a drying period of 28 days.

Viscosity

The viscosity was measured with a rotational viscometer with defined shear rate (ISO 3219-93). A Bohlin VOR rheometer with standard geometry and different torque bars was used for the measurements. The viscosity was measured over a large range of shear rates, but all samples showed Newtonian behaviour. The viscosity is given as a single value for each sample (see Table 2).

Results and Discussion

The oxidation rate

The oxidative drying was followed with real-time infrared spectroscopy (RTIR) to obtain information about the oxidation rate and the drying process. When studying the through-drying properties of an air-drying coating, it was convenient to follow the disappearance of the residual unconjugated cis-unsaturations in the drying oil which indicated the beginning of the oxidation process.

The decline of the peak at 3010cm⁻¹, corresponding to the symmetric stretching of the carbon-hydrogen bond in an unconjugated cis-unsaturation (cis-C=C-H), is well known¹³⁻¹⁵ to indicate the starting point of the oxidation process (see Figure 1).^{16,17} The total disappearance of the peak at 3010cm⁻¹ indicated that there were no residual unconjugated cis-double bonds left.

The spectral information in the ATR set-up was collected from the layer closest to the ATR-crystal (ie the bottom layer of the coating), where a complete disappearance of the peak at 3010cm⁻¹ can be related to a through-dried system. Surface sealing will severely slow down the through-drying because it results in a slower oxygen diffusion rate through the film, leaving non-reacted oil at the bottom of the film.

The influence of reactive diluents

The use of reactive diluents in the air-drying linseed oil systems have been evaluated. To decrease the viscosity of oils, it is possible to introduce reactive diluents. Reactive diluents are molecules with solvent-like properties that ultimately become part of the polymer net-

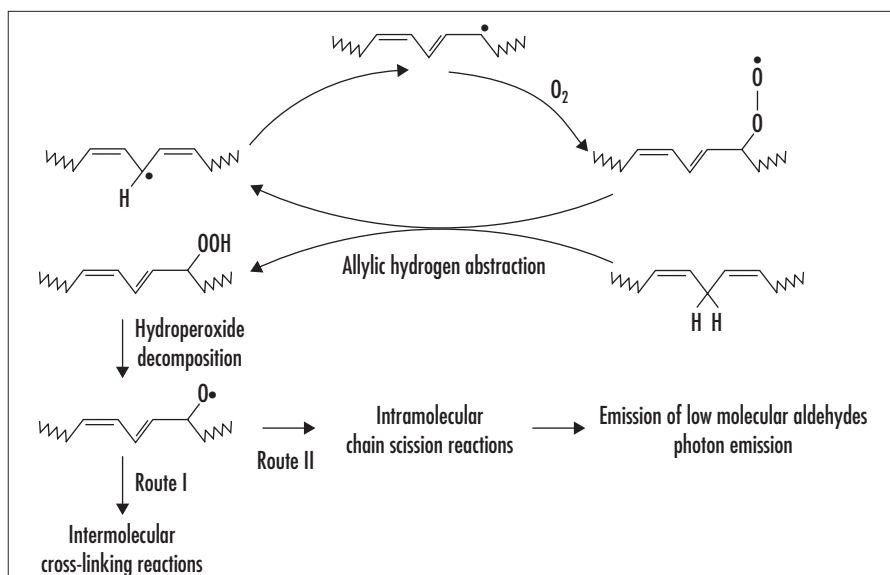


Figure 1: The oxidation process

work during cross-linking when the coating is drying. Reactive diluents require low volatility and high reactivity with the drying oils.^{12,18}

Fatty acid methyl esters of oil A were used as a reactive diluent, containing mostly methyl linoleate (see Figure 2). It was mixed with oil A and oil B to a content of 20, or 40wt%, of reactive diluents.

Viscosity measurements performed on the different oil formulations showed that the viscosity was decreased without the need of organic solvents when the fatty acid methyl ester of oil A was added (see Table 2).

RTIR-measurements showed that the slight addition of reactive diluents (20%) decreased the levels of residual unconjugated *cis*-double bonds (3010cm^{-1}) to approximately zero in oil B (see Figure 3). For oil A where the problems with residual *cis*-unsaturations were very low, very little additional decreases were seen (see Figure 4).

For oil B, the result can be related directly to the through-drying performance because the problem with surface sealing was decreased even at very low added levels of the reactive diluent.

The addition of reactive diluents changed the infrared absorbance profile. The fatty acid methyl ester can either react as wanted, with the oil by intermolecular addition reactions, or by unwanted intramolecular scission reactions generating volatile species. The presence of a non-reacted fatty acid methyl ester is also a drawback because non-reactive species with low volatility will remain in the drying oil and act as plasticisers. This affects the final properties of the coating, especially the hardness of the final film. When the fatty acid methyl ester was added to oil A and oil B, it gave rise to slightly softer final films.

Pendulum hardness data (see Table 3) show low values, which become even lower with time. This is explained by the influence of the properties of the glass substrate. When the film is through-dried, the glass does not affect the pendulum hardness. As long as the film is not completely dried, the hard surface of the glass will generate higher results because of the influence from the glass.¹¹ The very low hardness values also make it difficult to reveal significant differences between the dried films. A more appropriate method to study the final film properties of through-dried films could be indentation tests because this will be less affected by the substrate.

Chemiluminescence (CL)

The drying was also followed by chemiluminescence (CL) measurements. CL

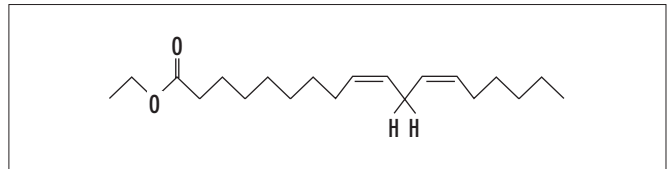


Figure 2: The major fatty acid methyl ester of the reactive diluent – methyl linoleate

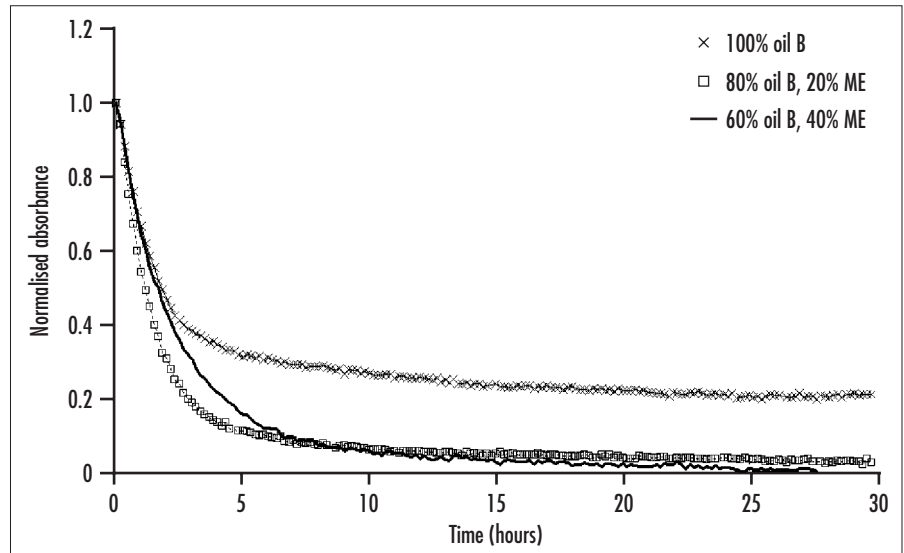


Figure 3: Change of absorption of unconjugated *cis*-unsaturations at 3010cm^{-1} (RTIR) with time for oil B, samples 4a to 6a, with a content of 0, 20 or 40wt% reactive diluents

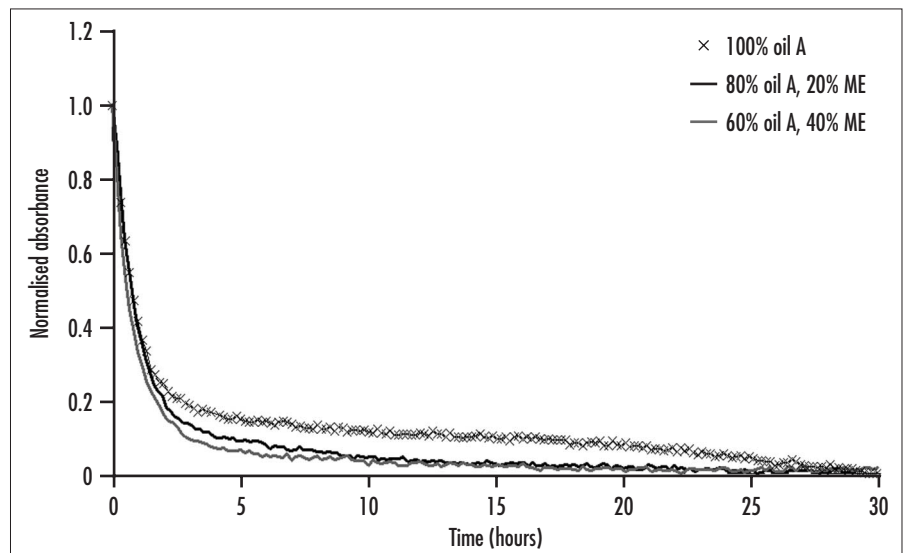


Figure 4: RTIR absorbance profiles at 3010cm^{-1} for samples 1 to 3 (oil A with 0, 20 and 40% reactive diluent)

Table 3: Pendulum hardness data

Sample	Content	Film hardness after 48 hours	Film hardness after 240 hours	Film hardness after 384 hours
1	100% oil A	25	11	10
2	80% oil A with 20% RD	26	11	4
3	60% oil A with 40% RD	7	13	16
4	100% oil B	14	11	9
5	80% oil B with 20% RD	16	10	7
6	60% oil B with 40% RD	6	7	12
7	40% oil A, 40% oil B and 20% RD	18	8	7

measurements on the pure oils as well as an evaluation of the method using chemiluminescence to follow the oxidation routes of the oils have been evaluated at various temperatures and presented in an earlier study.¹⁹

In this study, when a methyl ester of oil A was added as a reactive diluent to the oils, the profile of the photon emission changed. The photon emission increased, and the time before maximum emission was reached slightly increased as well (see Figures 5 to 8). The reaction routes were affected by introducing a reactive diluent. A probable explanation of this is found in the complex drying mechanisms of the oils, with the competitive reactions between cross-linking reactions (see Figure 1, route I) and the scission reactions (see Figure 1, route II). The probability of a scission reaction would increase when the methyl esters are present because this is an intramolecular reaction not affected by the overall structure. The addition reaction will be affected because an addition between two methyl esters would be less probable compared with an intramolecular reaction between two fatty acids in a triglyceride. When the concentration of reactive diluent (mainly methyl linoleate) becomes higher, the reaction rate of the competitive unwanted oxidative cleavage reaction becomes more dominating compared with the wanted intermolecular cross-linking reactions. This reasoning is also in accordance with emission studies made by Fjällström *et al*²⁰ on the same oil blends used in this study. The results showed a raised emission of hexanal when adding the methyl ester of oil A as the reactive diluent. Oxidative cleavage (ie β -scission reactions between C11 and C12 in the linoleate chains) is the most probable reason why hexanal is the major leaving aldehyde. The same cleavage product, hexanal, is also the major leaving aldehyde for oil A. For oil B, the major leaving aldehyde is propanal. Methyl linoleate (ie the reactive diluent) increases the emission of hexanal when it is added to both oil A and oil B. The fact that oil A and B emit mainly hexanal and propanal, respectively, shows that the scission reactions take place mainly at the terminal double bonds. In the present study, the CL results show higher emissions of photons (see Figures 5 to 8) with increasing amounts of reactive diluent added to the oils (ie more scission reactions).

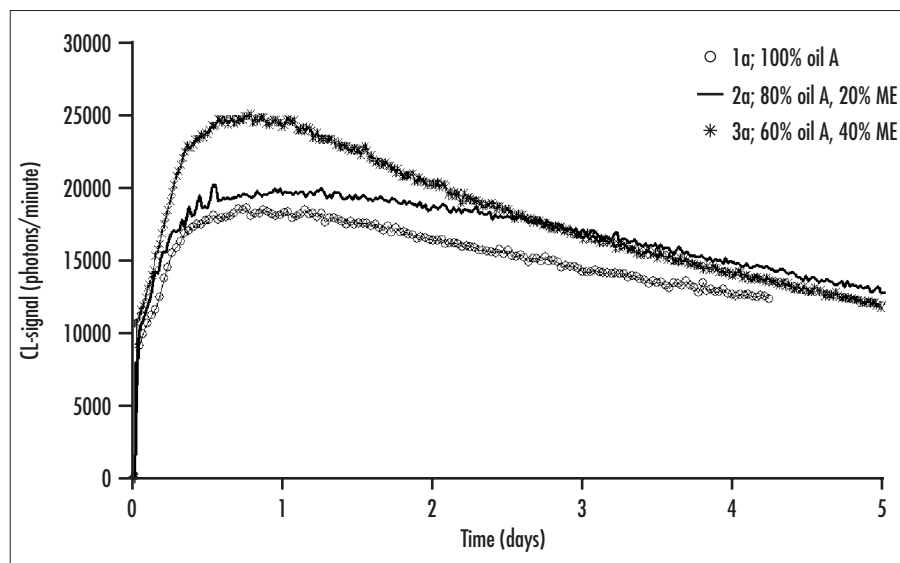


Figure 5: CL result for 1a to 3a (oil A + 0, 20 and 40% reactive diluent) on aluminium substrate

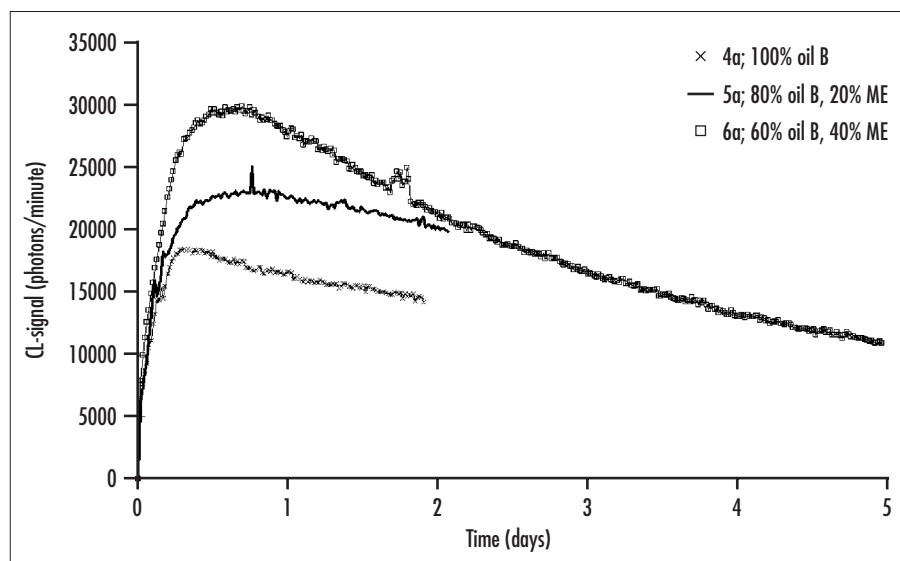


Figure 6: CL result for 4a to 6a (oil B + 0, 20 and 40% reactive diluent) on aluminium substrate

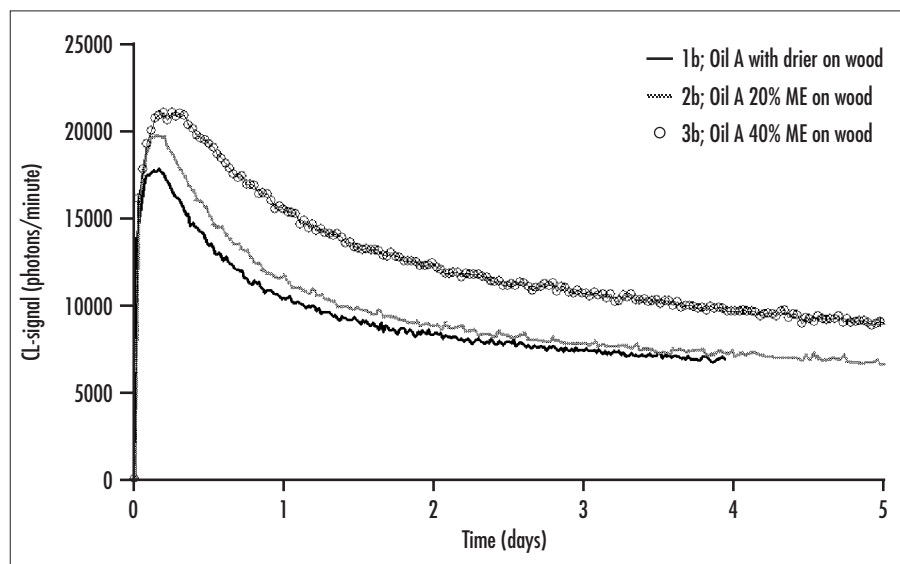


Figure 7: CL results for 1b to 3b (oil A + 0, 20 and 40% reactive diluent) on wood substrate

The effect of a wood substrate on the oxidative drying

The chemical reactivity between oil and wood is difficult to study because wood is a non-transparent solid with a complex morphology and chemical composition. One specific question to answer is if any of the wood constituents react chemically with the linseed oil or affect the oxidative drying of the linseed oils. Pizzi and Watson conducted some measurements indicating the possibility of chemical interference between linseed oil and wood.²¹ The possibility of using the CL technique for a simple but qualitative evaluation of the oxidative drying reactions of such complex systems was therefore briefly investigated.

In Figures 9 and 10, the relative effect on the drying rate is measured for oil A and oil B on a pinewood substrate with and without driers added.

There are many consequences of these results. It shows that the oxidative drying is accelerated in the contact between the wood substrate and the linseed oil. These results also show that the choice of substrate has a significant effect on the drying process for oils. The drying of linseed oil on wood seems to be chemically surface-activated (see Figures 9 to 12). Therefore, the oil must be in good contact with the surface. Surface initiation also normally induces a good stability and adhesion between the coating and the substrate. The results from these CL measurements do not reveal how active the surface is. It can be speculated that the activation of the oxidation from the surface also would have a great effect on the ability of the oil to penetrate deep into the wood structure. The higher the reactivity of the oil, the less the oil will penetrate the wood. It finally shows that results obtained on systems dried on other substrates than wood might be misleading.

The results clearly showed a much shorter induction period for the oxidation reactions when oil A and oil B were applied to the pinewood substrates (see Figures 9 to 12).

Emission studies on different types of substrates can also give hints about the reactivity with the substrate. High emission levels of low molecular aldehydes and carbonyl species are a result of intramolecular scission reactions instead of intermolecular cross-linking reactions. Fjällström *et al* performed emission studies on linseed oil with different substrates.²² The results showed the lowest emissions from wood substrates compared with other materials such as glass,

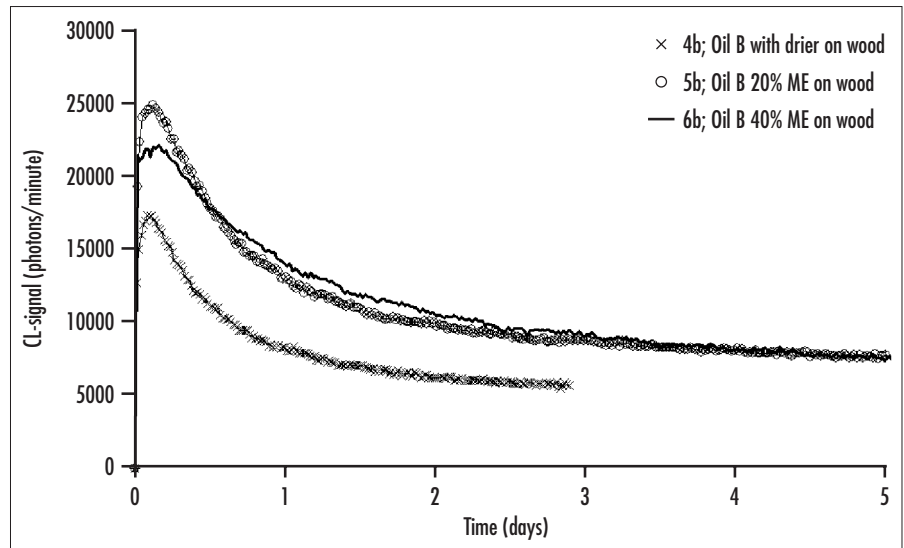


Figure 8: CL results for 4b to 6b (oil B + 0, 20 and 40% reactive diluent) on wood substrate

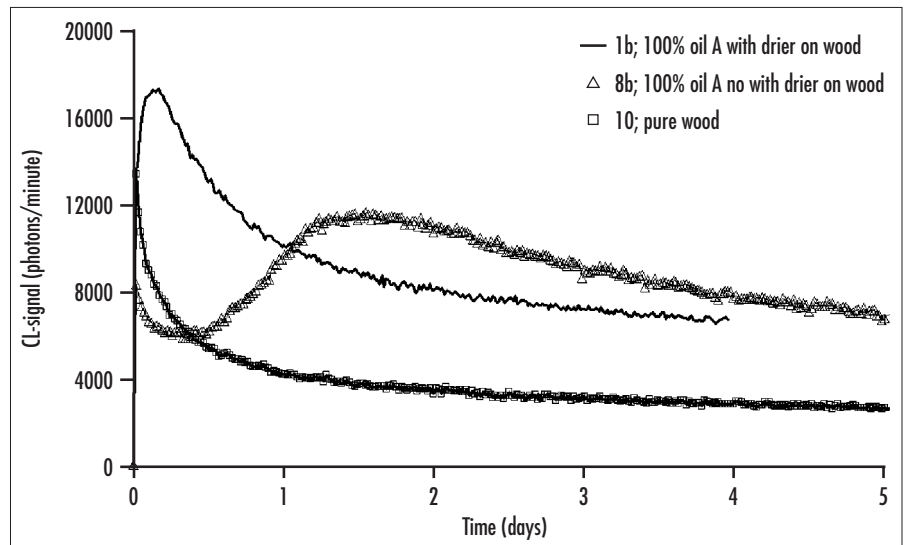


Figure 9: The influence of driers. CL results at 70°C on wood for oil A, samples 1b, 8b and 10

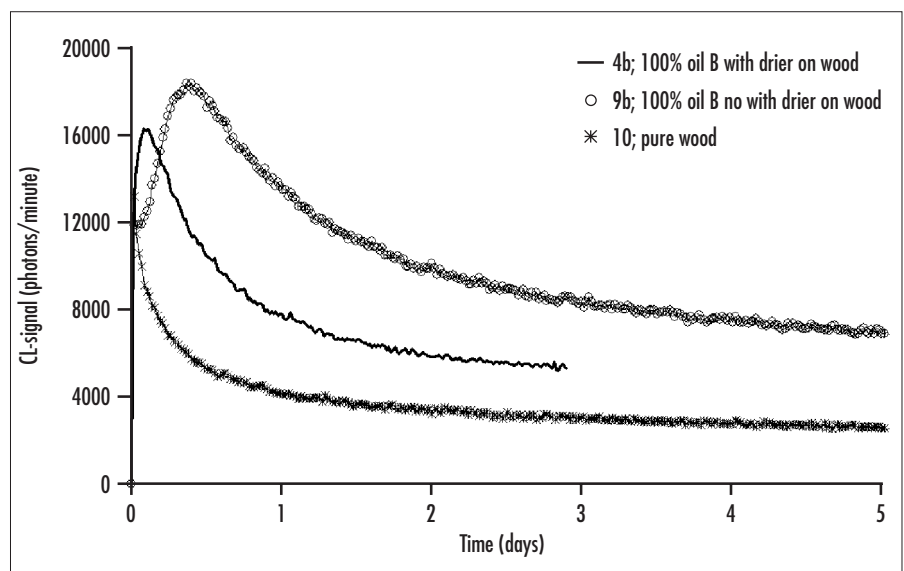


Figure 10: The influence of driers. CL results at 70°C on wood for oil B, samples 4b, 9b and 10

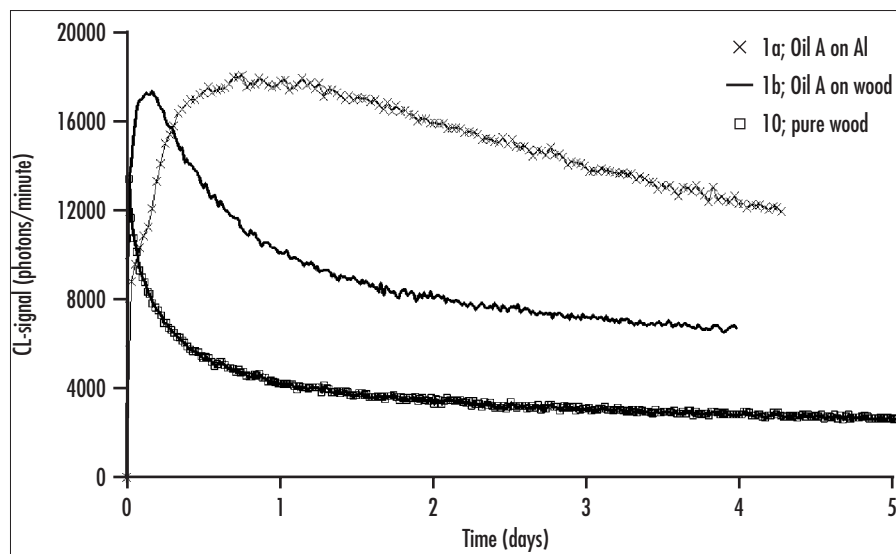


Figure 11: CL results at 70°C with driers for oil A, samples 1a, 1b and 10 varying the substrate

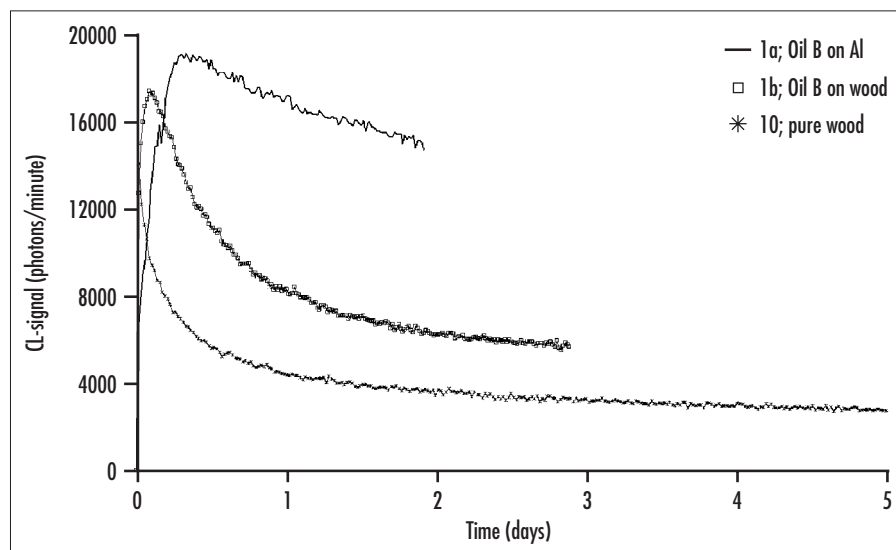


Figure 12: CL results at 70°C with driers for oil B, samples 4a, 4b and 10 varying the substrate

fibreboard, gypsum board and lime mortar. This supports the results found in this study that the wood itself triggers the auto-oxidation process.

Conclusions

The introduction of the fatty acid methyl ester of a linseed oil as a reactive diluent to wood oils based on linseed oil gives softer films, but offers the possibility of lowering the use of volatile organic compounds (VOCs). The reactive diluent lowers the viscosity and reacts upon drying with the oils forming a coating on the substrate. For oil B, rich in linolenic acid, the reactive diluent lowered the risk of surface sealing and the amount of residual unsaturations in the final coating. Photon emissions increased with increased amounts of fatty acid methyl ester in the oil formulations. An explanation for this observation is the competing

inter- and intramolecular reactions of the hydroperoxides formed during the oxidation process, leading to cross-linking versus scission reactions emitting low molecular species and photon emissions as a consequence.

Pine wood substrates are seen to affect the drying rate for the oils. The CL results show a significant shorter induction period for the oxidation reactions when the oils are drying, even without the use of a drier when they are applied on wood substrates. To approach similar results when oils were applied to an aluminium substrate, it was necessary to use a commercial metal salt mixture as a drier. The results imply that there is a demand for further studies on how different wood materials affect the oxidative drying process. Not only the viscosity but also the chemical reactivity will, for example, affect how well certain oils penetrate

into a wood substrate. More reactive oils may be suitable for some wood substrates, whereas less reactive oils will be preferred for other wood materials.

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