



**KTH Fiber- och  
polymerteknologi**

# Influence of the fatty acid pattern on the drying of linseed oils

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AKADEMISK AVHANDLING

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## LIST OF PAPERS

This thesis is a summary of the following papers:

- 1 “A study of the drying of linseed oils with different fatty acid patterns using RTIR-spectroscopy and Chemiluminescence (CL)” *Accepted in Industrial Crops and Products (2004)*
- 2 “Drying of linseed oil wood coatings using reactive diluents” *To be submitted to Surface Coatings International Part B: Coatings Transactions (2004)*

## ABSTRACT

The interest in renewable resources due to environmental factors has increased the interest to use new VOC-free linseed oil qualities together with reactive diluents for coating applications. The drying of two linseed oils, Oil **A** with a high content (74,2 %) of linoleic acid (C18:2) and oil **B**, a more traditional linseed oil with a high amount (55,2-60,4 %) of linolenic acid (C18:3), was followed in order to reveal how the structural variations of the oils fatty acid pattern and the addition of the fatty acid methyl ester of oil **A** as a reactive diluent (0, 20 40 wt%) can change the drying performances of the oils and their final film properties.

The influence of the drying temperature and the influence of driers was investigated. The drying performance of the different oil formulations applied on pinewood substrates was briefly investigated. Two different analytical techniques, chemiluminescence (CL), and real-time infrared spectroscopy, (RTIR), were shown to be versatile tools for the analysis of the drying process. Chemiluminescence is shown to be a useful technique to follow oxidative drying measurements on wood.

The final properties of the dried film, depends on the fatty acid composition of the oil. Linseed oil (oil **B**) high in linolenic acid (C18:3) has more problems with residual unconjugated cis-unsaturations in the drying film. Surface sealing effects were achieved when driers were added, or when the reaction temperatures were increased. The "skin" will act as a diffusion barrier for oxygen and further drying. The drying then proceeds at a very slow rate, leading to residual unconjugated cis-unsaturations affecting the long-term durability and the colourfastness. Reaction rates are influenced for both wanted intermolecular cross-linking reactions building up the polymer matrix, and unwanted intramolecular degradation reactions, leading to volatile emission of low molecular species as well as photon emission from the auto-oxidation process.

The incorporation of reactive diluents, fatty methyl esters of oil **A** reduce the effects of surface sealing for oil **B** at higher temperatures and therefore increase the oxidative drying rate. Slightly softer final coatings are obtained. The drying of oil **A** does not tend to be as sensible as for oil **B** to driers and raised temperatures, but the addition of reactive diluents influences the final coating properties giving softer final coatings.

CL-measurements when oil **A** and oil **B** were applied to pinewood substrates resulted in shorter induction periods for the oxidation reactions. It shows that the oxidative drying is influenced by a chemical reactivity between the wood substrate and the linseed oils. This would have a great affect on the ability of the oil to penetrate deep into the wood structure. The higher the reactivity of the oil, the lesser the oil will penetrate the wood. These results greatly improve the possibility to produce a coating for wood protection with acceptable properties using oils high in linoleic acid with fatty acid methyl esters added as reactive diluents.

This shows that studies on other substrates than wood might be misleading.

# SAMMANFATTNING

Det ökande intresset för förnyelsebara råvaror av miljöskäl har ökat intresset för användandet av nya linoljor fria från lösningsmedel, tillsammans med reaktiva spädare för ytbehandling av trä. Den oxidativa torkningen av två linoljor med olika fettsyramönster, olja **A** med hög halt (74,2 %) av linolsyra (C18:2) och en mer traditionell typ av linolja, olja **B** med hög halt (55,2-60,4 %) av linolensyra (C18:3) har studerats under olika torkningsbetingelser för att få en ökad förståelse av hur fettsyramönstret och tillsatser av metylestrar av olja **A** som reaktiva spädare (0, 20, 40 vikt %) kan påverka torkningen av oljorna och de torkade filmernas slutegenskaper. Torkningsförloppets påverkan av torktemperatur och tillsatser av torkmedel, s.k. sickativ har studerats. En ytlig undersökning av hur de olika blandningarna av oljor påverkas av trä som substrat har också genomförts.

Två olika analysmetoder, infraröd spektroskopi i realtid (RTIR) och kemiluminescens (CL) har visat sig vara bra analysverktyg för att följa torkningen av linoljor.

Kemiluminescens har också visat sig vara en användbar metod för att följa oljors torkning på trä.

Den torkade filmens slutegenskaper är beroende av oljans fettsyramönster. Linolja (olja **B**) med hög halt av linolensyra (C18:3) har mer problem med kvarvarande restomättnader av okonjugerade cis-omättnader i den torkande filmen. En ytförseglingseffekt uppstår då sickativ tillsätts eller då torktemperaturen ökas. "Ytskinnet" bildar en diffusionsbarriär mot syre och vidare torkning. Torkningen sker då mycket långsamt. Kvarvarande restomättnader av okonjugerade cis-omättnader ( $3010\text{cm}^{-1}$  i RTIR) påverkar långtidsegenskaperna hos den torkande linoljan negativt. Den torkande filmen kan gulna och spricka. Reaktionshastigheten hos både de önskade intermolekylära tvärbindningsreaktionerna, som bygger upp den färdiga filmens tredimensionella nätverk, och oönskade intramolekylära nedbrytningsreaktioner, som leder till både emission av lågmolekylära ämnen, och emission av fotoner påverkas. Tillsatser av reaktiva spädare, metylestrar av olja **A**, minskar effekten av ytförsegling hos olja **B** vid förhöjda torktemperaturer. Torkningshastigheten ökar då för olja **B**. De torkade filmerna blir något mjukare då reaktiva spädare används. Torkningen av olja **A** påverkas inte i samma utsträckning av förhöjda temperaturer och tillsatser av sickativ som olja **B**. Tillsatser av reaktiva spädare påverkar dock den torkade filmens sluthårdhet. Den torkade filmen blir mjukare.

Kemiluminescensmätningar visar att olja **A** och olja **B** båda får kortare induktionstid och alltså torkar snabbare då oljorna appliceras på trä. Resultaten visar att den oxidativa torkningen påverkas av den kemiska reaktiviteten mellan trä och linolja. Det här påverkar också oljans förmåga att tränga in i träet. En olja med alltför hög reaktivitet stanna kvar på ytan där den torkar. Dessa resultat ökar kraftigt förhoppningen om att det är möjligt att tillverka en linolja baserad på höga halter linolsyra (C18:2) med tillräckliga torkegenskaper som är fri från lösningsmedel. Istället kan reaktiva spädare av linoljans metylestrar tillsättas.

Det här visar också att torkningsstudier på andra substrat än trä kan leda till felaktiga slutsatser om oljans torkegenskaper på trä.

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# 1 INTRODUCTION

## 1.1 Purpose of the study

The interest in renewable resources due to environmental factors has increased the interest to use new linseed oil qualities together with reactive diluents for coating applications [1]. The purpose of this licentiate thesis has primarily been to reveal how structural variations in the fatty acid pattern of linseed oil, and secondly how the influence of fatty acid methyl esters used as reactive diluents, can change the drying performance and the final film properties for linseed oil based coatings. The reactive diluents were added in order to avoid VOC's (volatile organic compounds). Two different analytical techniques, chemiluminescence (CL), and real-time infrared spectroscopy (RTIR), were chosen to follow the oxidative drying behaviour of the linseed oil formulations. The drying performance of the linseed oil formulations on a wood substrate was briefly investigated.

## 1.2 Background

### *1.2.1 Vegetable oils in general*

Vegetable oils are triglycerides i.e. esters of glycerol combined with three fatty acids. The fatty acids could be the same or different with varying hydrocarbon chain length, and varying amount of double bonds (Figure 1). The hydrocarbon length varies from 10 to 20 carbon atoms including the carbon atom in the acid group (-COOH). Depending on the fatty acid pattern, vegetable oils can be divided into non-drying, semi-drying and drying oils. Non-drying oils contain mostly saturated fatty acids, which are unable to react to form a cross-linked film by air oxidation. The presence of double bonds increases the oil's reactivity to form a solid, coherent and adherent film when spread on a surface, as the double bonds are able to polymerise (cross-link) when exposed to oxygen. Semi-drying oils contain fatty acids with only one or two double bonds, for instance soybean oil, sunflower oil, tall oil or safflower oil. Drying oils are highly unsaturated oils, consisting of fatty acids containing two or three double bonds. Linseed oil and tung oil are examples of drying oils [2].

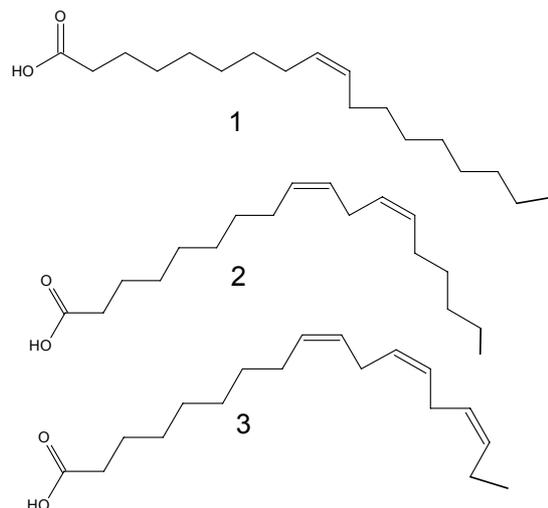


Figure 1: Structures of common fatty acids in linseed oil: **1** Oleic acid, **2** Linoleic acid, **3** Linolenic acid

The drying oils will form a tack-free film over a period of time whereas semi-drying oils form films that never become completely tack-free. An oil is traditionally considered to be a drying oil when the level of unsaturations in the oil is high enough i.e. if the average number of methylene groups between two double bonds per molecule is greater than 2,2 [3].

Commercially exploited seeds, such as soya, rapeseed, sunflower and linseed, have been the subjects of many years of breeding programmes to obtain oils with particular fatty acid patterns [4-7]. In addition to breeding efforts of these traditional oil crops, work is being done to domesticate alternative oil rich plants that may yield new potentially useful fatty acids [1, 8-10].

In recent years, genetic engineering approaches have been considered to make particular fatty acids or introducing new fatty acids in available crops [9, 11]. This may, in the future, lead to an even greater range of drying oils available for the coating industry and an increased need for basic studies of the drying properties of fatty acids and their esters.

### 1.2.2 Linseed oil

The fatty acid pattern of linseed oils can have a natural variation depending on the climate where the crops were grown, the quality of the linseeds, possible genetic variations of the crop and how the raw oil is being refined [9]. The drying process is fairly slow even with a drying oil such as raw linseed oil. By pre-polymerisation of the raw oil, an increase of the molecular weight and viscosity is achieved, which improves the overall film forming properties, especially the drying time.

### 1.2.3 The production of linseed oil

Raw linseed oil is produced by expression or solvent extraction of linseed or flax (*Linum usitatissimum*). It contains variable amounts of impurities, such as free fatty acids, phospholipids, carbohydrates and antioxidants. To precipitate the impurities, the raw oil needs to be degummed and refined by treatment with acid or alkali. Further modification of the oils by pre-polymerisation further improves the drying properties of the oils (Figure 2). Several processes can be used to achieve pre-polymerised linseed oils such as blown oil, stand oil and boiled oil [9, 12].

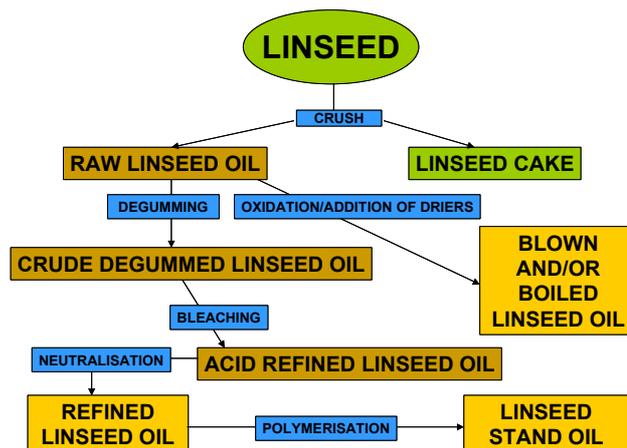


Figure 2: The refining and pre-treatment procedures of raw linseed oil

Heating the raw oil under an inert gas to around 160-300 °C produces heat-polymerised oils, heat-bodied oils or *stand oils*. The heating might be carried out in the presence of peroxides to further improve the cross-linking. The viscosity of the heated oil increases continuously during the whole heating process. If the oils are heated under thermal control at about 130 °C and oxidised at the same time by blowing air through the oil they are called *blown oils*. If catalysts are used they are usually added in the form of driers. *Boiled oils* are produced from linseed oil using one or more driers to accelerate the pre-polymerisation. They are traditionally processed by a controlled oxidation of raw linseed oil by heating the oil to a temperature of about 250 °C. The oils are called boiled oils even though the cooking temperature is below the boiling and decomposition point.

#### 1.2.4 Wood protection

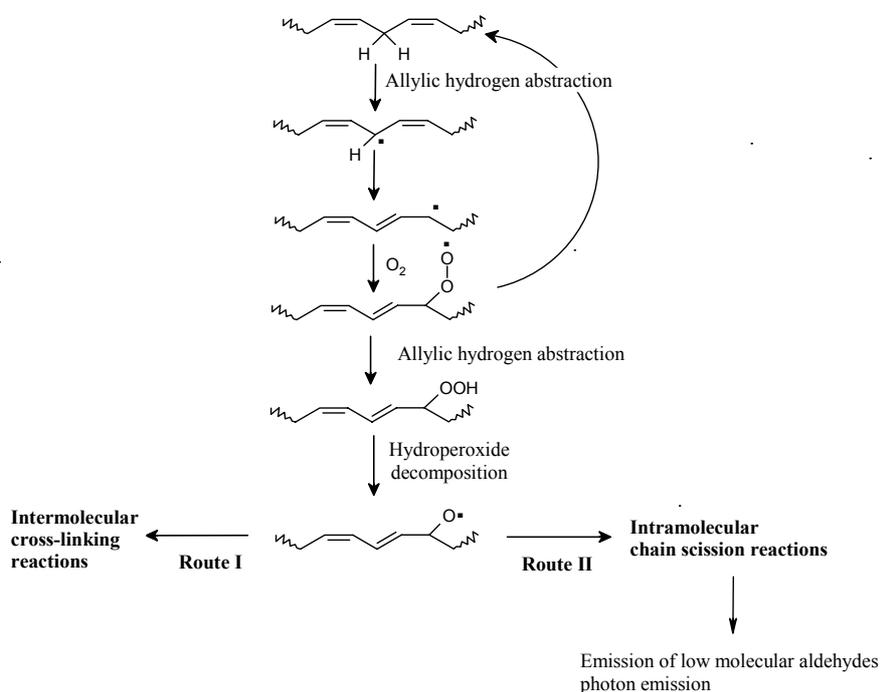
The performance of a coating on wood is controlled by various stressing factors such as the presence of moisture and microorganisms causing different weathering effects and in outdoor applications factors such as photo irradiation, thermal radiation, mechanical impact etc. The degree of degradation is very much influenced by the quality of the wood properties, the wooden structure and moisture content [13, 14]. Properties of the coating material are also important, such as the viscosity of the coating material affecting the penetration into the wood as well as the polarity, the chemical reactivity between wood and the coating and the thickness of the coating. All these variables have an influence on the final result.

### 1.3 The drying process

The overall drying mechanism of drying oils is very complex with several competing reactions that differ depending on reaction conditions and oil structure. Many studies have been performed in order to achieve better understanding of the auto-oxidative drying mechanisms [15-22]. Generally, it could be described to include an induction period, followed by the uptake of oxygen and finally, a polymerisation stage involving cross-linking, the liberation of volatile oxidation products and the formation of the dried film [2].

### 1.3.1 Mechanism of auto-oxidation

The auto-oxidation of linseed oil is the direct reaction of molecular oxygen with the oil and proceeds by a free radical chain mechanism [19, 20].



*Scheme 1: The mechanisms of the auto-oxidation of unsaturated fatty acids*

It consists of a complex series of reactions. The auto-oxidation mechanism, schematically described in Scheme 1, is initiated by hydrogen abstraction from unsaturated fatty acids containing allylic centres. The allylic radical formed undergoes rearrangements and will react either with other radicals or, more probably, with molecular oxygen due to its availability and high concentration. The reaction with oxygen results in the production of hydroperoxides, which will decompose when heated or irradiated. The decomposition can also be catalysed by metal salts i.e. driers [23-26].

### 1.3.2 *Drying*

The chemical reactions following the decomposition of hydroperoxides will either lead to intermolecular cross-linking or intramolecular chain scission. The drying process occurs when formed alkoxy radicals either add to double bonds or couple with other free radicals (Route I in Scheme 1). The addition/coupling reactions must dominate over the scission reactions (Route II in Scheme 1) to obtain drying. This is achieved when the level of unsaturations in the oil is high enough i.e. when the oil is defined as a drying oil.

Fragmentation reactions will however occur (Route II in Scheme 1). There are two dominating mechanistic explanations for scission reactions,  $\beta$ -scission and the Russell mechanism [27]. Secondary alkoxy radicals may undergo decomposition by  $\beta$ -scission, which leads to emission of low molecular species such as aldehydes. The practical consequences of these scission reactions are the well-known odours when linseed oils are drying.

### 1.3.3 *Driers or siccatives*

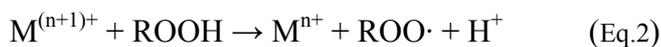
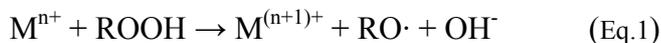
The oxidative drying of vegetable oils is a rather slow process that can be accelerated by the addition of transition metal salts as catalysts, so called driers. Driers based on cobalt and lead, were added to unsaturated oils such as linseed oil as early as the end of the 19<sup>th</sup> century [23]. The metal driers in common use can be divided into two broad classes based on their main interaction with the air-drying system. A side effect of driers is that their action continues throughout the service life of the coating film, thus accelerating the ageing of the organic material [15]. This is shown as a brittleness and breakdown of the coating film.

#### 1.3.3.1 *Primary driers (top driers)*

Primary driers are also referred to as top driers or catalytic driers. They contain transition metals with several oxidation states such as cobalt and manganese salts, which in small amounts (0.005 % to 0.2 % metal, based on the oil) catalyses the formation and/or decomposition of peroxides formed by the reaction of oxygen with the drying oil [2]. Free

radicals are formed and the formation of direct polymer-to-polymer cross-links (top drying) becomes possible.

The following reaction mechanism (Eq. 1 and 2) called the Haber and Weiss mechanism has been proposed [2, 24].



The main function of primary driers is to promote rapid surface drying of air-drying coatings but they do also have to some extent through-drying properties.

### 1.3.3.2 Secondary driers

The second type of driers is so called cross-linking driers or through-driers. Used alone, these driers do not have any large catalytic effect on the oxidation process. Though in combination with primary driers they act as synergist and increase the rate of oxygen uptake in air-drying systems considerably. Modern oil systems for air-drying coatings usually contain a mixture of different driers to obtain the right balance of top drying and through drying.

A mixture of driers could also include auxiliary driers, which further promotes the through drying and improve the stability of the primary driers used. Examples of metals used in commercial through-driers are zirconium, aluminium, and barium salts. Common auxiliary driers are based on potassium and calcium salts.

## 1.4 Real-time infrared spectroscopy RTIR

Several studies have shown that real-time IR spectroscopy (RTIR) is a powerful technique to monitor the drying of unsaturated fatty acid structures [26, 28-30]. The absorption bands in the infrared spectra represent different structural parts in the drying oil. Time resolved spectra give information of chemical changes during the initial oxidation process (Figure 3).

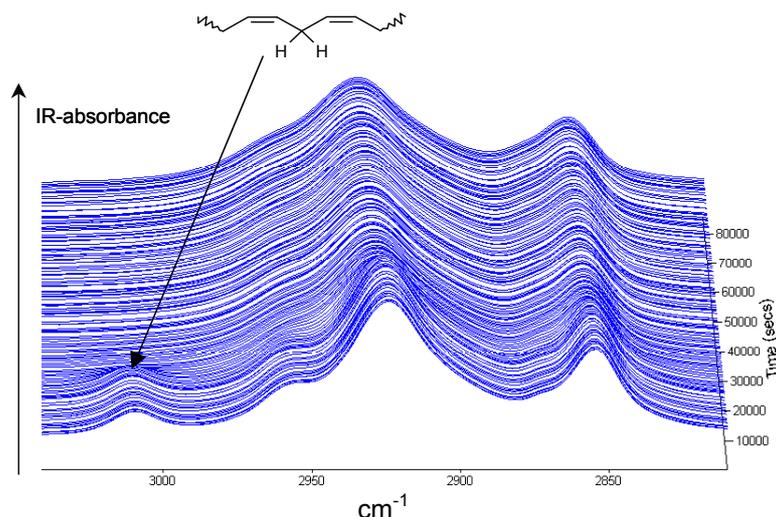


Figure 3: Detail from a time resolved infrared spectra of the drying of a linseed oil. Changes in the absorption band at  $3010\text{ cm}^{-1}$  related to unconjugated cis-unsaturations as a function of time, can easily be monitored.

Absorption bands that are relevant to the oxidation process can be monitored as a function of time following their intensity changes as shown in Figure 3.

To be able to monitor the initial auto-oxidative drying mechanism of the oils, certain absorption bands are more important than others. The most interesting bands [31] are those involved in the initiating rearrangements of the unconjugated cis-double bonds ( $3010\text{ cm}^{-1}$ ) to conjugated trans-double bonds ( $990\text{ cm}^{-1}$ ) further to unconjugated trans-unsaturations ( $970\text{ cm}^{-1}$ ). The RTIR-time resolved spectra make it possible to follow the drying. While the unconjugated cis-unsaturation disappears (RTIR,  $3010\text{ cm}^{-1}$ ) the formation of conjugated trans double bonds (RTIR,  $990\text{ cm}^{-1}$ ) appears. Very soon these conjugated trans double bonds are consumed according to Scheme 1, mainly leaving isolated double bonds (RTIR,  $720, 970\text{ cm}^{-1}$ ), see Figure 4. These results are also shown in RTIR–studies on model oils conducted by Johansson et al [32].

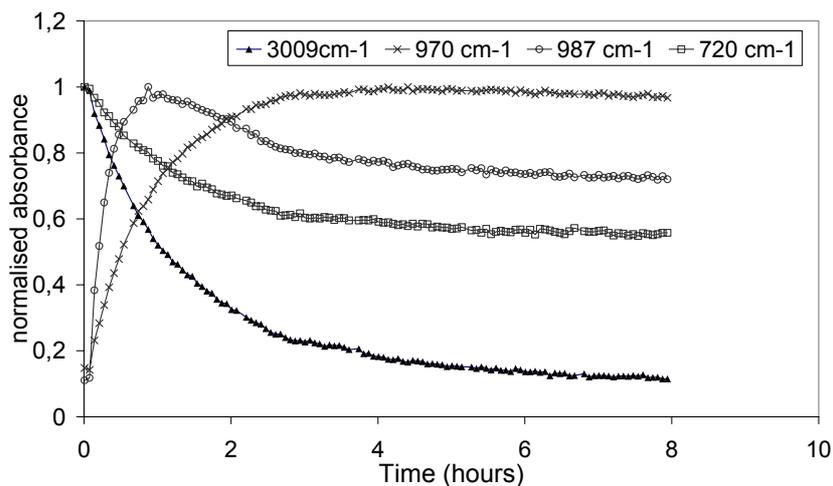


Figure 4: RTIR traces at 720, 970, 987 and 3009  $\text{cm}^{-1}$  for a linseed oil drying at 70  $^{\circ}\text{C}$  with a top drier added (0.1 % Cobalt metal).

The studies with real time IR spectroscopy can be performed either by measuring the IR absorption through an entire film in transmission or as Attenuated Total Reflection (ATR) measurements on the surface of an ATR-crystal. Transmission measurements will yield spectra representing an average of the chemical changes throughout the film while spectra from ATR measurements only represent the changes in the thin layer close to the ATR crystal (Figure 5).

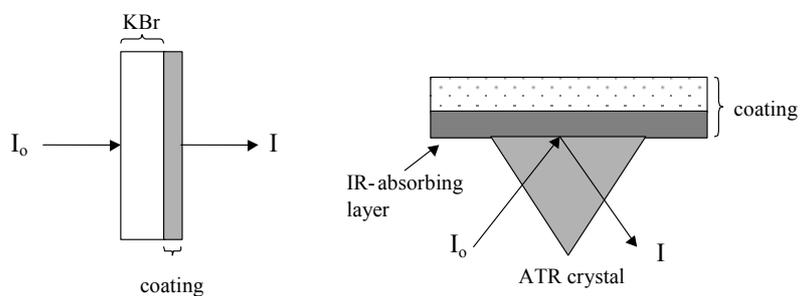


Figure 5: Principles of transmission measurements and attenuated total reflection (ATR) measurements

Both IR- techniques have limitations that have to be considered when evaluating the data [28]. Reactions in a thin and outermost layer can be rather large and still not detectable in transmission mode. The result of the transmission measurements that gives an average absorption through the whole film will give very little information about the drying at the surface when measured on a very thick film. ATR measurements on the other hand, only detect changes close to the bottom of the coating film i.e. the part of the coating in contact with the ATR-crystal. If reactions in the surface region create diffusion barriers towards atmospheric oxygen, the rate changes in the IR measurement will be decreased. In the present study we have chosen to employ the ATR technique.

### 1.5 Chemiluminescence CL

Free radical oxidation of polymers and organic compounds leads to emission of low levels of visible light, photons, which is commonly termed as chemiluminescence (CL) [33]. CL-measurements can be used to follow oxidation reactions in real-time with high sensitivity. The development of photon counting techniques has improved the possibility to study the polymer oxidation by measuring the amount of photons emitted. This has made chemiluminescence a suitable analytical technique for studies of polymer degradation [33, 34]. During CL-measurements in oxygen-containing atmospheres the oxidation continues. Therefore, the CL-emission may be regarded to quantify the degree of oxidation [35]. During the oxidation process, it is believed that excited carbonyl groups are generated. When these carbonyls relax it emits photons. The reactions responsible for the formation of this excited carbonyl group is not completely understood. Decomposition reactions are believed to be responsible in the drying film. Blakey and George [36] present two possible chemiluminescence mechanisms associated with auto-oxidation for the explanation of formation of light emission. These are termination of peroxy radicals via the so-called Russell mechanism, and the decomposition of hydroperoxides. In CL analysis the signal results from measuring the entire test sample and its average drying but only a part of the oxidation process.

## 2 EXPERIMENTAL

Detailed experimental data can be found in papers I and II.

### 2.1 Materials

#### 2.1.1 Oil formulations

In the first study, oils from two different varieties of linseed (*Linum usitatissimum*) have been prepared, analysed (Svalöf Laboratory, Svenska Lantmännen) and supplied by Svenska Lantmännen (Sweden). The oils were obtained by cold crushing of the linseeds followed by refining of the raw oil at with bleaching earth and filtration. Seeds were sown and harvested in Sweden during 1999. Both oils had very low concentrations of free fatty acid (<1 mg KOH/g) and phospholipids (P <1 ppm). Oil **A** (Purolin®) originates from an edible variety of linseed and has a large content of linoleic acid (C 18:2). Oil **B** originates from a traditional variety of linseed and has a large content in linolenic acid (C18:3). In the second paper, methyl esters of oil **A** (Linutin®) are used as reactive diluents. Oil **B** (oil **B2** in Table 1), with a slightly changed fatty acid pattern from the first study was supplied by Svenska Lantmännen (Sweden) and refined by Solutia Denmark (Søborg, Denmark). The concentration of phospholipids in oil **B2** was changed to 5 ppm. The fatty acid patterns of the reactive diluent and the different oils are presented in Table 1. All chemicals were used without further purification.

*Table 1: The fatty acid composition (%) of linseed oils A and B. The oils mainly differ in the content of the reactive fatty acids i.e. linoleic (C18:2) and linolenic (C18:3) acid.*

Fatty acid	C16: 0	C16: 1	C18: 0	C18: 1	C18: 2	C18: 3	C20: 0	C20: 1	>C:20
Oil <b>A</b>	6.0	0.1	3.3	13.0	<b>74.2</b>	2.7	0.1	0.4	
Oil <b>B</b>	5.1	0.1	3.5	13.4	16.8	<b>60.4</b>	0.1	0.4	
Oil <b>B2</b>	5,0		3,3	19,3	14,6	<b>55,2</b>			2,6
Reactive diluent methyl ester of oil <b>A</b>	6.0	0.1	3.3	13.0	<b>74.2</b>	2.7	0.1	0.4	

*Driers and sample formulations*

Two drier systems have been used. For the first model study, a primary drier (a top drier), Co-2-ethyl-hexanoate, Co-10 HEX-CEM (10 wt-% Cobalt) from OMG Europe (Dusseldorf, Germany) was solitary chosen and mixed with pure oil **A** and **B** respectively to give a total Co-metal content of 0.1 %. Tests were performed both with and without drier added to oil **A** and **B**.

In the second study, a commercial mixture of a primary drier, Co-10 HEX-CEM (10 wt-% Cobalt) from OMG Europe (Dusseldorf, Germany) a through-drier Zr-18 HEX-CEM with 18wt-% of Zr metal (OMG, Germany) and an auxiliary drier Octa-Soligen Calcium 10 (Borchers GmbH, Langenfeld, Germany) with 10 wt-% of Ca was used. When the drier mixture was added to the oil blends the metal content was 0.0024 wt-% Co-metal, 0.0034 wt-% Zr-metal and 0.0040 wt-% Ca-metal, i.e. a total metal content of 0.01 wt-%. The different samples are listed in Table 2.

*Table 2: The composition of the formulations, evaluated in the studies on the addition of reactive diluents. (The fatty acid pattern of oil **B** is presented as oil **B2** in table 1).*

Sample	Oil content (RD = reactive diluent)	Drier (Co:Zr:Ca)	Viscosity (mPas)
<b>1</b>	100% Oil <b>A</b>	Total of 0.01%	69,0
<b>2</b>	80% Oil <b>A</b> and 20% RD	Total of 0.01%	39,6
<b>3</b>	60% Oil <b>A</b> and 40% RD	Total of 0.01%	26,6
<b>4</b>	100% Oil <b>B</b>	Total of 0.01%	59,0
<b>5</b>	80% Oil <b>B</b> and 20% RD	Total of 0.01%	40,8
<b>6</b>	60% Oil <b>B</b> and 40% RD	Total of 0.01%	25,2
<b>7</b>	40% Oil <b>A</b> , 40% Oil <b>B</b> and 20% RD	Total of 0.01%	41,0
<b>8</b>	100% Oil <b>A</b>	No drier	-
<b>9</b>	100% Oil <b>B</b>	No drier	-
<b>10</b>	0 % (100 % pine heartwood lath)	-	-

### 2.1.2 Substrates

In the first model study (paper I), oil was applied on an aluminium pan (diameter 20 mm) for the chemiluminescence measurements. In the real-time infrared spectroscopy measurements the samples were all applied on the ATR-crystal device. Two different substrates were used in the extended study (paper II) using reactive diluents, the aluminium pan and Swedish pine heartwood lath plates (supplied by Växjö Universitet, Växjö, Sweden). Wooden plates sized 200 × 100 × 8 mm (longitudinal, radial, tangential directions) were cut out with a saw into wood plates with a size of 20 × 20 × 8 mm (longitudinal, radial, tangential directions). The small plates were finally split in two halves (20 × 20 × 4 mm) in order to fit in the CL apparatus. The oils were applied on the splint side, in 45° to the radial direction, on the wood substrates. The oil formulations are denoted with **1a-9a** corresponding to aluminium or **1b-9b** corresponding to wood as the substrate when presenting the results of the CL-measurements.

## 2.2 Techniques

### 2.2.1 Real-time infrared spectroscopy (RTIR)

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 (30, 70 or 100 °C). When the chosen temperature was established on the ATR-accessory, the oil sample (5-10 µl) was applied onto the ATR-crystal, leaving an oily thin film. The surrounding atmosphere was air. The IR-measurements were commenced directly after the oil was applied and spectra were recorded every 5 or 10 minutes depending on the total running time. The software used to collect and present data was Timebase®, from Perkin-Elmer.

### 2.2.2 Chemiluminescence (CL)

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 was applied directly on an aluminium test plate or applied on top of wood substrates, and then placed in a

temperature- and airflow-controlled test-chamber inside the CL-apparatus. Before inserting the samples, the desired temperature (30, 70 or 100 °C) in the test chamber was well established. As soon as vacuum was received around the test chamber the counting of emitted photons was started. Data was collected once a minute. The atmosphere in the chamber was controlled by a constant airflow 60 ml/min during the whole experiment. This made it possible to run comparable experiments in both RTIR and CL, following the auto-oxidation reactions in real time.

### 3 RESULTS AND DISCUSSION

In paper I, the oxidative drying of two oils with controlled fatty acid composition was studied.

Earlier works by Mallegol, Muizebelt and others [24, 37, 38], have shown that both the temperature and the drier have an influence on the oxidation process of drying oils. The main purpose of this work was to reveal how controlled variations in the fatty acid pattern together with increased curing temperature could influence the oxidative drying and the final properties of the dried film. Suitable techniques, RTIR and CL were chosen to verify the results. It has previously been shown that the combination of these techniques, give a good overall description of the oxidation of fatty acids [32]. The aim of the second work was to expand the studies to get better understanding of how fatty acid methyl esters could influence the drying rate and the properties of the final coating and at the same time act as a reactive diluent minimising the need of volatile solvents. Research conducted on the volatile emission from the drying of linseed oils by Fjällström et al. [39], has shown that the substrate also could affect the oxidation process. Hence, a brief study with pinewood as a substrate was performed. The results from these measurements showing the influence of reactive diluents and the use wooden substrates are presented in paper II.

#### 3.1 A study of oils with different fatty acid pattern

The structural differences between linoleic acid (C18:2) and linolenic acid (C 18:3) suggest that oils with a higher fraction of linolenic acid oxidise (dry) more rapidly, could be cross-linked more densely and give harder films [3].

##### 3.1.1 *Influence of the temperature*

Oil A, containing mainly linoleate esters, follows an expected dependency with temperature for the non-catalysed system. The oxidation reaction is accelerated with increased temperature. RTIR results, clearly show a shorter induction time for the drying of oil A at higher temperatures when the disappearance of unconjugated cis-unsaturations ( $3010\text{ cm}^{-1}$ ), during of the oxidative drying is followed (Figure 6). The results also show a

very low level of residual cis-unsaturations in the test samples, at all temperatures. The dried films show no tendency towards skin formation and wrinkling.

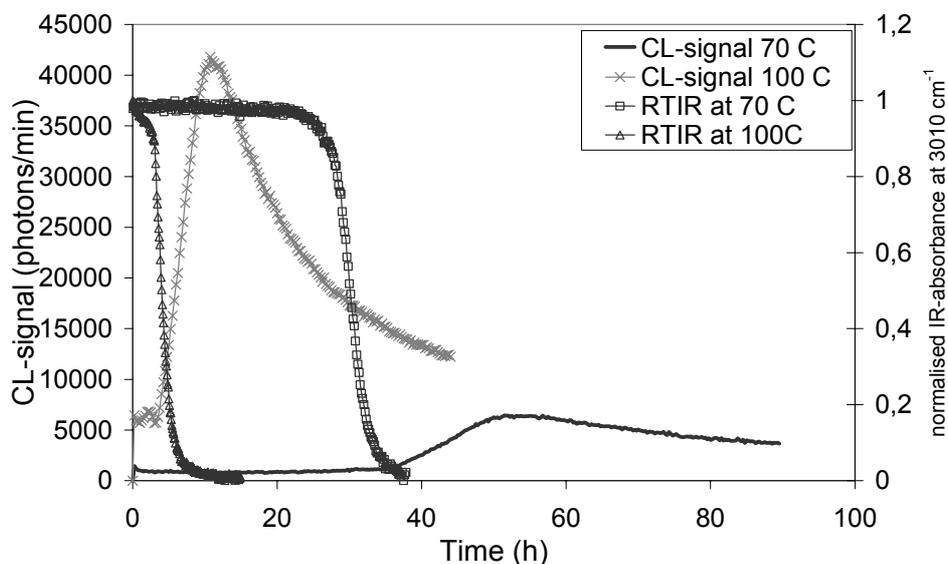


Figure 6: CL-signal and the change of absorption at  $3010\text{ cm}^{-1}$  (RTIR) with time for oil **A** at  $70\text{ }^{\circ}\text{C}$  and  $100\text{ }^{\circ}\text{C}$ .

These results indicate that the auto-oxidative drying only is accelerated with raised temperature and that no diffusion barriers are formed. The correlation between CL and RTIR measurements has been evaluated in previous studies [32], showing that chemiluminescence emission does not start until conjugated trans double bonds (RTIR  $970\text{ cm}^{-1}$ ) are consumed, i.e. addition is the predominant reaction in the presence of conjugated double bonds. The complete disappearance of unconjugated cis-unsaturations (Figure 6) before any CL-emission is seen, suggests that the first stage of the oxidation mainly give rise to cross-linking (Route I, Scheme 1) rather than chain scission (Route II, Scheme 1).

CL-measurements show that a raised temperature generates a stronger CL-signal but also a fast decrease of the signal, i.e. the drying goes faster. For oil **B**, having a large content of linolenic acid, an increased temperature for the uncatalysed oxidative drying results in an

increased rate and stronger CL-signal in the same way as for oil **A**, though the onset of oxidation is much more rapid and proceeds at a higher rate than oil **A** (Figure 7). No tendency to skin formation or wrinkling is seen.

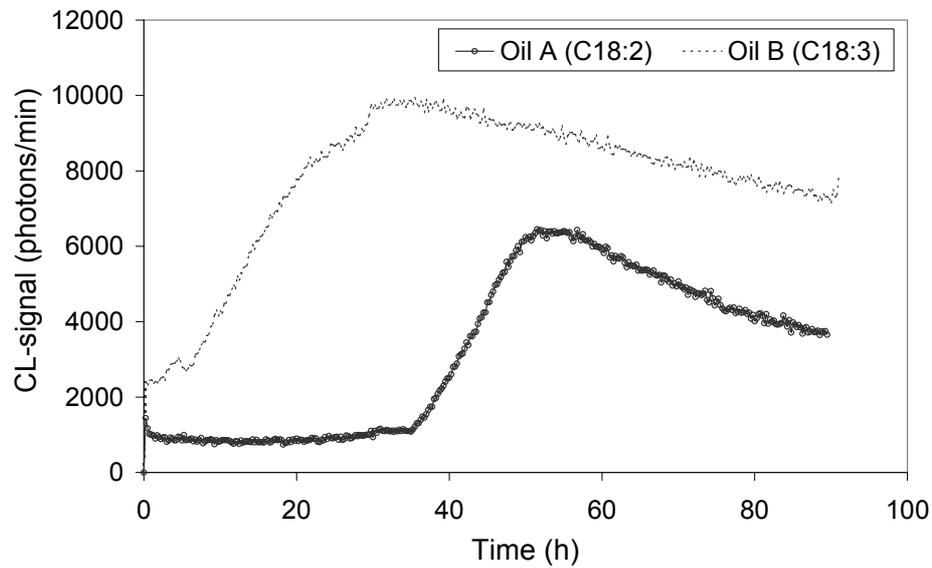


Figure 7: CL-signal at 70°C for oil **A** and oil **B** without driers added.

### 3.1.2 Influence of driers

The addition of driers accelerates the decomposition of hydroperoxides according to Eq. 1, formed during the oxidation of the oils. This accelerates the drying of both oil **A** and oil **B** in the same way but the final properties of the dried films will be different. Measurements done on oil **A** (C 18:2) show that the CL-signal becomes stronger with increased temperature and that the photon emission also starts earlier (Figure 8). This confirms that the use of a drier increase the overall reaction rate and that it also increases the possibility for unwanted scission reactions to some extent.

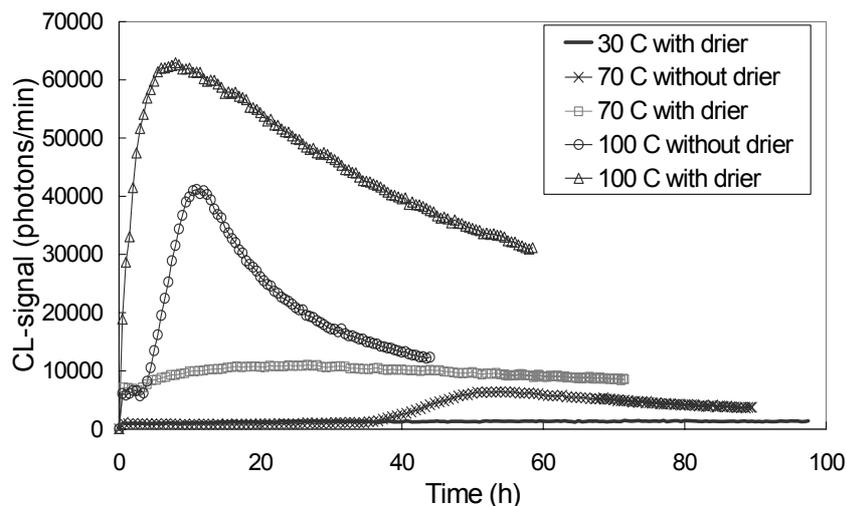


Figure 8: CL-emission as a function of time for oil **A** at 70 °C and 100 °C without a drier added, compared to CL-emission at the same temperatures with a drier added to oil **A**.

The residual amount of unconjugated cis-unsaturations (RTIR 3010  $\text{cm}^{-1}$ ) decline to very low levels in all experiments with oil **A**, both with and without driers added, suggesting a good long-term stability which is seen in the RTIR measurements (Figure 9). The films of the rapidly cured samples of oil **A** with driers added, show some wrinkles indicating a slightly too fast surface curing, generating a sparse network not dense enough to inhibit diffusion of oxygen through the surface. The wrinkling is though significantly less compared to films based on oil **B** cured at the same conditions.

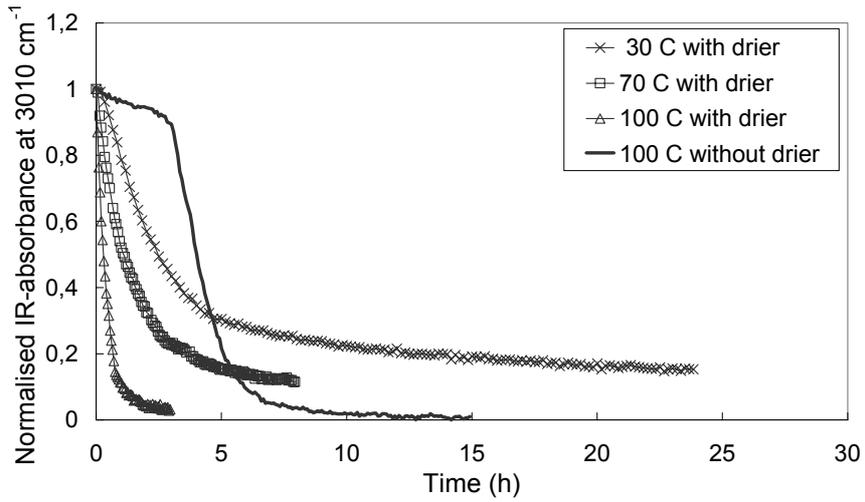


Figure 9: Changes in the absorption band at  $3010\text{ cm}^{-1}$  related to unconjugated cis-unsaturations as a function of time for oil **A** (C 18:2)

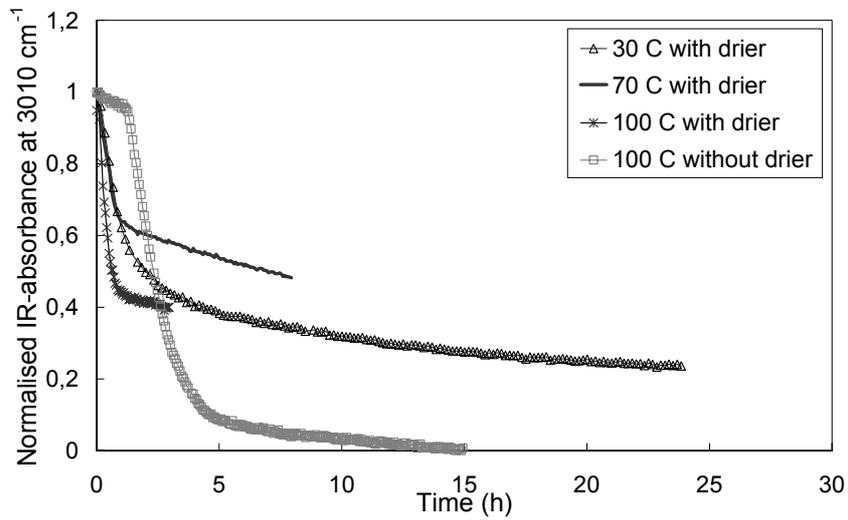


Figure 10: Changes in the absorption band at  $3010\text{ cm}^{-1}$  related to unconjugated cis-unsaturations as a function of time for oil **B** (C 18:3).

For oil **B** (C18:3) the addition of a drier increases the initial drying rate significantly minimising the induction time of the auto-oxidation. RTIR measurements show a faster decrease of unconjugated cis-unsaturations (at  $3010\text{ cm}^{-1}$ ), at higher temperatures, but it also results in higher levels of residual unconjugated cis-unsaturations (Figure 10).

This suggests that the reaction becomes diffusion dependent at a certain stage i.e. a skin is formed with a dense network at the top limiting the diffusion of oxygen to the bottom of the film. In the RTIR results for oil **B** it is seen that the lowest temperature ( $30\text{ }^{\circ}\text{C}$ ) result in the lowest amount of residual unsaturations in the bottom layer. When the temperature is increased to  $70\text{ }^{\circ}\text{C}$ , it results in a higher initial oxidation rate due to the presence of the top drier (the cobalt salt) mainly active in the surface layer of the drying film but also a more abrupt stop of the oxidation. This is probably related to the formation of a “skin” with a  $T_g$  in the range of this temperature. Increasing the temperature further to  $100\text{ }^{\circ}\text{C}$  also results in an abrupt stop but at lower level of residual unsaturations. This lower level may be due to the fact that a temperature high enough makes the film softer which reduces the barrier function of the “skin”.

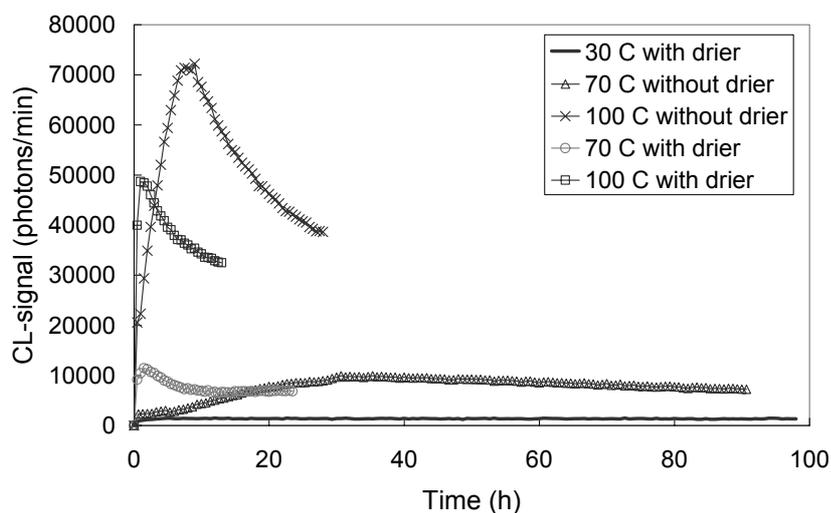


Figure 11: CL-signal as a function of time for oil **B** (C18:3)

CL results for oil **B** (Figure 11) could be compared to the obtained results of oil **A** (Figure 8) supporting this theory. The addition of a drier causes the CL-signal to appear earlier. At

higher temperatures, the intensity of the signal is decreased when a drier is present. This is opposite to the trend for oil **A** and suggests that the oxidation reactions are limited by barrier (skin) formation.

The conclusion is that it is difficult to increase the drying rate above a certain limit for oils with high content of linolenic acid, without the risk of poor through drying and skin formation, generating wrinkles in the dried film.

In paper II, a commercial drier mixture (Co: Zr: Ca) was chosen to improve the through-drying properties, but the effect of surface sealing at higher drying temperatures was still observed for oil **B**. Oil **A** does not show the same surface sealing tendency as oil **B**.

### 3.2 Influence of reactive diluents

The use, and the subsequent emission of volatile organic compounds (VOC's), has been increasingly considered as an environmental problem. More than 95 % of the exterior wood coatings are applied as liquid coatings with either organic solvents or water as the carrier for the other coating ingredients. A general strategy of the paint industry is to replace solvent-borne paints by low-VOC alternatives [40]. To reduce the viscosity of the oil during application it is possible to introduce reactive diluents. Reactive diluents are molecules with solvent-like properties that ultimately become part of the polymer network during cross-linking when the coating is drying. Reactive diluents require low volatility and high reactivity with the drying oils [41, 42].

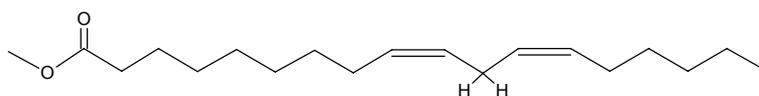


Figure 12: The major fatty acid methyl ester of the reactive diluent - methyl linoleate

In paper II, the use of reactive diluents in air-drying linseed oil systems has been evaluated. Fatty acid methyl esters of oil **A** were used as a reactive diluent, containing mostly methyl linoleate (Figure 12). It was mixed with oil **A** and oil **B** to a content of 20 or 40 wt-% reactive diluents. The viscosity of the oils was then reduced without the need of organic solvents (Table 2). CL-measurements on the oils were run at 70 °C. The CL-

emission increased when reactive diluents were added to both oil **A** and to oil **B** (Figure 13).

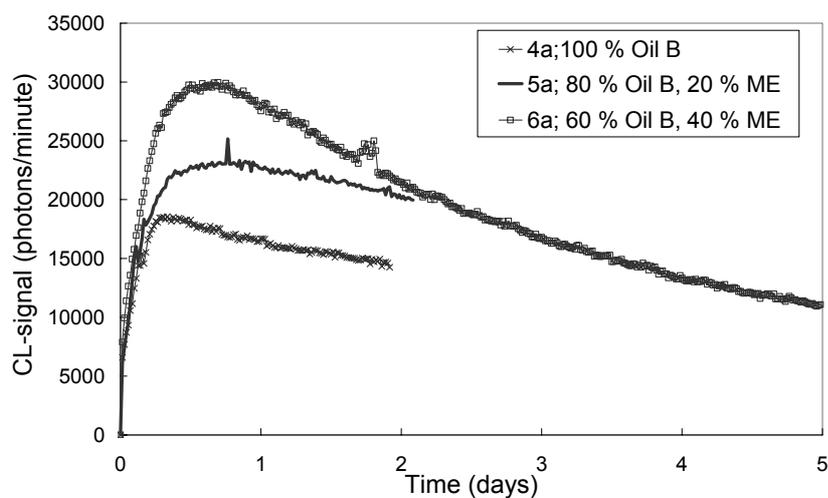


Figure 13: CL-results from the drying of oil **B** at 70 °C containing 0, 20 or 40 wt-% reactive diluents (samples 4a-6a).

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 unreacted fatty acid methyl ester is also a drawback since 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 is added to oil **A** and oil **B** it give rise to slightly softer final films. Pendulum hardness results in paper II show low values for both oil **A** and oil **B**. In a parallel study that was performed by Andersson et al. [43], the emission of volatile organic species from the oxidative drying of oil **A** and **B**, was measured. When reactive diluents based on the fatty acid methyl esters of oil **A**, were added to both oil **A** and oil **B**, an increased amount of aldehydes was emitted. The largest increase of the volatiles was detected to be hexanal, most probably due to  $\beta$ -cleavage between C-12 and C-13 in the linoleate chain. The increase of the CL-signal is therefore proposed to be a consequence of the increased probability of intramolecular scission reactions of the fatty acid methyl esters.

RTIR-measurements show that a slight addition of reactive diluents (20 %) reduces the levels of residual unconjugated cis-double bonds ( $3010\text{ cm}^{-1}$ ) to approximately zero in oil **B** (Figure 14). For oil **A** where the problems with residual cis-unsaturations are very low, very little additional reduction effects are seen.

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

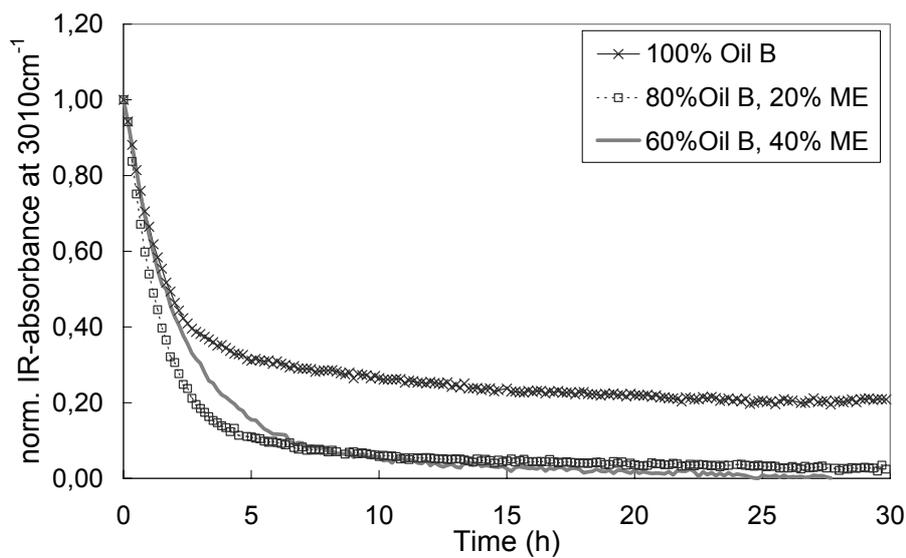


Figure 14: Change of absorption at  $3010\text{ cm}^{-1}$  (RTIR) with time for oil **B**, sample **4a-6a**, with a content of 0, 20 or 40 wt-% reactive diluents.

The need to add reactive diluents to oil **A** only concerns the need to lower the viscosity of the formulation to avoid volatile solvents. For oil **B** though, it is necessary for the improvement of the through drying properties. Very small effects on the amount of residual unsaturations are seen for oil **A**. These results also indicate that the fatty acids have similar reactivity irrespectively if they are a part of a triglyceride or a methyl ester.

### 3.3 The effect of substrate

The use of linseed oil as a wood primer has a long tradition. An important aspect is the linseed oil's ability to penetrate into the wood while drying to protect wood and serve as a good coating. The depth of the penetration depends on several factors [44]. The viscosity of the oil is one, others factors that will have an influence are the wood composition, the polarity, and the chemical reactivity. The chemical reactivity between oil and wood is difficult to study since 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 reacts 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 [45]. The possibility to use the CL-technique for a simple but qualitative evaluation of the oxidative drying reactions of such complex systems was therefore briefly investigated.

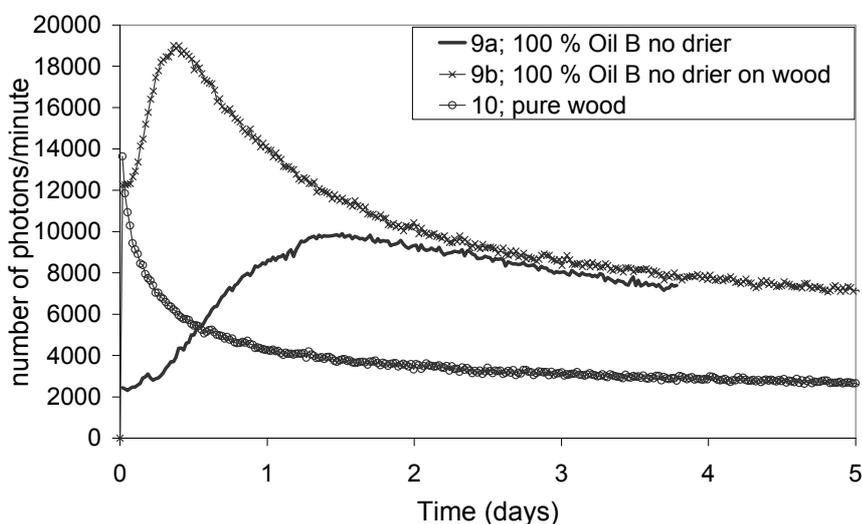


Figure15: The increase of the CL-signal and the faster oxidation rate for oil **B** when pinewood is used as the substrate.

The results clearly showed a much shorter induction period for the oxidation reactions when oil **A** and oil **B** was applied to the pinewood substrates. The effect of wood as a

substrate is exemplified by the results from measurements of the CL-emission when oil **B** is drying on different substrates, aluminium and pinewood without the influence of a drier, shown in Figure 15.

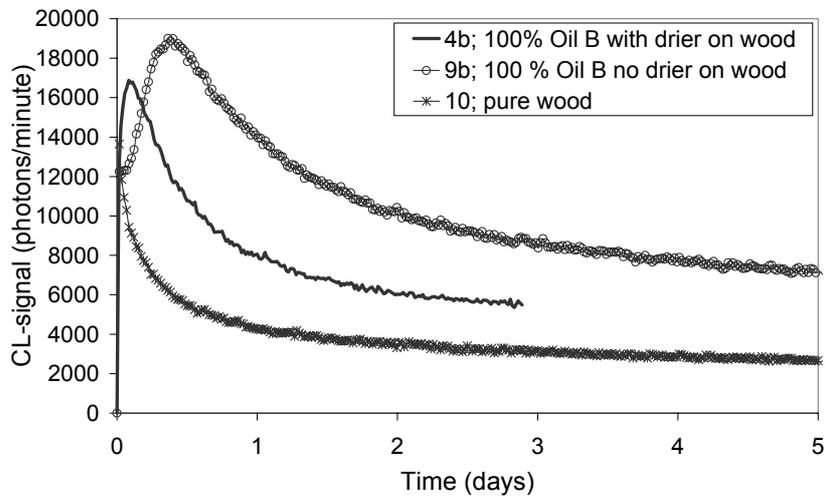


Figure 16: CL-results at 70 °C (samples 4b, 9b and 10) showing the relative effect of the drying rate with and without a drier added when oil B is dried on a wood substrate.

In Figure 16, the relative effect on the drying rate is measured for oil **B** on a pinewood substrate with and without a drier 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. 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 in that the activation of the oxidation from the surface also would have a great affect on the ability of the oil to penetrate deep into the wood structure. The higher the reactivity of the oil, the lesser the oil will penetrate the wood. It finally shows that results obtained on systems dried on other substrates than wood, might be misleading.

Volatile emission studies performed by Fjällström et al. [39] on different types of substrates also give hints about the reactivity of the oils with the substrates. In the emission studies on different substrates, Oil **A** was applied on glass, pinewood, fibreboard, gypsum board etc.

The lowest emissions of low molecular volatile species were achieved with pinewood as the substrate. This supports the results from the study in paper II, that wood is involved in some reactions (that needs more research studies to be further explained) that may trigger the wanted intermolecular cross-linking reactions of the auto-oxidative drying.

These results also show that it is possible to use a linseed oil with high levels of linoleic acid in the fatty acid pattern together with reactive diluents to lower the viscosity, avoiding volatile organic compounds and still get a wood coating with good coating properties.

## 4 CONCLUSIONS

Traditional linseed oil based coatings can be improved with respect to their properties by changing the fatty acid composition. The drying behaviour is influenced both by the addition of driers and raised drying temperatures. The final properties of the dried film, depends on the fatty acid composition of the oil. Reaction rates for both wanted intermolecular cross-linking reactions and unwanted intramolecular degradation reactions in the auto-oxidation process are influenced. Traditional linseed oils dominated by linolenic acid are shown to have more problems with residual unconjugated cis-unsaturations in the drying film explained by surface sealing effects, where the “skin” will act as a diffusion barrier for oxygen and further oxidative drying. The drying process then proceeds at a very slow rate, which will affect the long-term durability and the colourfastness.

Fatty acid methyl esters can be used as reactive diluents in drying oils, but their influence on the properties must be matched. The incorporation of the methyl ester of oil **A** as a reactive diluent into oil **B** reduces the effects of surface sealing at higher temperatures and therefore increase the oxidative drying rate for oil **B** but it will produce slightly softer final coatings.

The drying of linseed oils on wooden substrates of pinewood resulted in much shorter induction periods of the initial oxidative drying for both oil **A** and oil **B**. Chemical reactivity between wood and the oils or wood itself seem to trigger the oxidative drying. It is possible to produce a coating for wood protection with good properties when linoleic acid is the dominating fatty acid in the oil such as in oil **A**. These results also show that the choice of substrate has a significant effect on the drying process for oils.

Chemiluminescence (CL) and Real-time infrared spectroscopy (RTIR) are shown to be versatile tools for the analysis of the oxidative drying of vegetable oils.

Chemiluminescence is also shown to be a useful technique for measurements on complex substrates such as wood.

## 5 FUTURE WORK

The present study shows that the substrate has an influence on the oxidative drying of linseed oil coatings. Not only is the viscosity of the oil important for the penetration ability, so an extended study on different wood materials such as oak, pine to get deeper understanding of the oil penetration as well as chemical interactive reactions between the linseed oil systems and the wood material, focusing on the oxidation rate of linseed oil coatings, would be of great interest. Chemiluminescence (CL) measurements should be combined with magnetic resonance (MR) profiling. This method makes it possible to get a three dimensional picture of the oxidation process and the final film properties. Also, further studies on alternative driers such as manganese-drier systems, are environmentally interesting in order to avoid cobalt-metal in the oil-formulations without losing the good properties of linseed oil coatings used on wood.

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