



A study of the drying of linseed oils with different fatty acid patterns using RTIR-spectroscopy and chemiluminescence (CL)

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Abstract

The oxidative drying of two different linseed oil coatings with either high content of linoleic or linolenic fatty acids have been studied. The curing performance has been followed by a combination of two different analytical techniques, real-time infrared (RTIR) spectroscopy and chemiluminescence (CL) at different temperatures. The effect of a metal drier on the drying process has also been evaluated. The purpose was to reveal how structural variations can improve the drying performance and film properties for oxidative drying linseed oil coatings.

The reaction rate is increased for both oils with increased temperature as expected. The oil rich in linolenic acid reacts more rapid and exhibits shorter induction times compared to the oil rich in linoleic acid. The addition of a metal drier further accelerates the drying but in a different manner for the different oils. The oil high in linolenic acid oxidizes so rapidly that a skin layer, acting as a diffusion barrier to atmospheric oxygen, is formed. The through drying rate is then strongly reduced, leaving high levels of residual unsaturation in the film. As a consequence, this will generate poor ageing properties. The oil richness in linoleic acid shows, much better through drying properties even when the reaction is accelerated by both the use of a metal drier and high temperatures. The consequence is that the linseed oil high in linoleic acid can be cured rapidly with good through drying and low levels of residual unsaturations.

The combination of the two analytical techniques gives complementary information of the drying mechanisms of the linseed oils. The techniques are shown to be very useful when following oxidative drying of thin films.

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1. Introduction

Natural oils are esters of fatty acids and glycerol that are obtained from several oleochemical sources (animal, marine and vegetable). The use of the oil is determined by the composition of fatty acids, and this is highly dependent on its natural origin. Animal

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sources, e.g. lard and tallow, are characterised by high concentrations of saturated fatty acids, whilst marine sources (fish oils) are characterised by long chain and unsaturated acids. The fatty acid composition of oils from vegetable sources varies depending on plant origin and sort. Commercially exploited seeds such as soya, rape, sunflower and linseed have been the subject of many years of breeding programmes to obtain oils with particular fatty acid patterns. In addition to breeding efforts on traditional oil crops, work is being done to domesticate alternative oil-rich plants that may yield new potentially useful fatty acids (Derksen et al., 1996; Samuelsson and Johansson, 2001).

In recent years, genetic engineering approaches have been considered to make a contribution in expanding the available materials for “non-food” uses, such as increasing the concentration of a particular fatty acid or introducing new fatty acids. In the latter context, an abundance of unusual fatty acids can be found in plants from nature. These unusual fatty acids have been classified by Spitzer (Spitzer, 1999) according to the functionalities in the fatty acid chain, like acetylenic, allenic, epoxide, fluoro, and cyclopropene fatty acids. In some cases, the genes responsible for the synthesis of these have been identified and genetic engineering is under way to transfer the genes and express them in plants suitable for cultivation (Lee et al., 1998; Hill, 2000). 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 drying properties of fatty acids and their esters.

The general attention to materials from renewable natural products due to the interest in a sustainable development have increased the interest for products made with fats and vegetable oils during the last decades. Linseed oil has a long tradition as coating resin by itself, or modified in coatings such as alkyds (Wicks, 1986). The oil dries by an oxidation process usually catalysed with metal driers (Lazzari and Chiantore, 1999; Mallegol et al., 2000). The advantage with linseed oil is that it is a relatively inexpensive resource for drying oil and that it provides good protection of wood where the penetration ability of the oil into the wood is superior to other alternatives. However, there are disadvantages such as problems with yellowing, poor long-term stability and rather soft films. This has been the major reason

for the replacement of linseed oil by modern synthetic coatings such as alkyds and latex coatings in wood protection.

The improved knowledge by modern crop development on plant breeding and developed production techniques have introduced the possibility of designing the oil structure. This has resulted in linseed varieties with higher yields, controlled oil content and increased content of unsaturated fatty acids (higher iodine values). In recent years, a new line of plant breeding has been employed in order to obtain edible linseed oil, i.e. in which the concentration of the easily oxidised and unpalatable linolenic acid has been minimised (Green and Marshall, 1984; Green, 1987; Bhatti and Rowland, 1990). By removing as much as possible of this fatty acid, the risk for unpleasant rancidity products is reduced. However, this also leads to a reduced iodine value, hence, oil that may be regarded as unsuitable in paint and coating applications. In this paper, we describe how the oil rich in linoleic acid indeed can be used in protective coatings. If this type of linseed oil solves the mentioned problems it could increase the interest for the use of linseed oil.

1.1. The oxidation process

The drying of linseed oil is an oxidative process. It is well-known that both linoleate and linolenate structures oxidise rapidly since they contain double allylic hydrogen atoms that are easy to abstract in the auto-oxidation process (Frankel, 1980). Fig. 1 presents a general auto-oxidation scheme for a linoleate structure (Porter et al., 1995). When the formed hydroperoxides decompose they form species that either crosslink the system or induce chain scission. The optimal oil would contain reactive groups that promote crosslinking, rapidly react and leave low amounts of residual unsaturations to enable long time durability of the final coating.

The linoleate hydroperoxide contains mainly conjugated double bonds whilst the linolenate hydroperoxide contains both conjugated and unconjugated double bonds. The very complex reaction routes make it difficult to employ only one analytical technique to obtain a full picture of the reacting system. The oxidation process involves a chain of reactions of which some can be detected with one technique but not all.

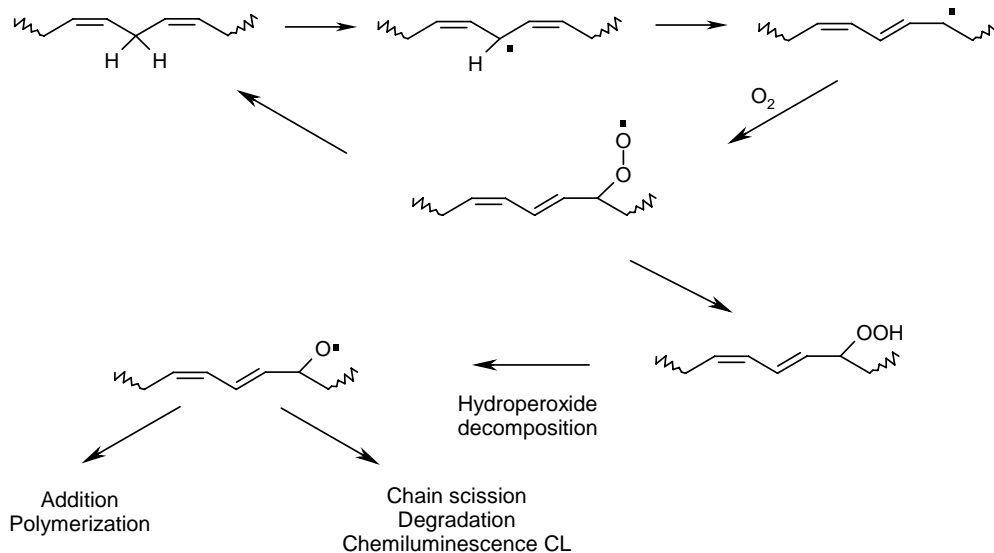


Fig. 1. Schematic description of the auto-oxidation process for a linoleate structure. The decomposition of the hydroperoxide leads to either scission or addition reactions.

Some steps might lead to the decomposition of the drying species, resulting in photon emission, generally referred to as chemiluminescence (CL) (Matisova-Rychla and Rychly, 1996; Matthaus, 1996). One suggested mechanism is the coupling of two peroxy radicals (ROO^\bullet) to form a tetroxide (ROOOOR), which when it decomposes results in photon emission, i.e. the Russel mechanism (Russel, 1957, pp. 3871–3877). Another mechanism proposes that the degradation of hydroperoxides (ROOH) formed in the auto-oxidation process will produce alkoxy radicals (RO^\bullet) (or similar reactive species) that in a second step will lead to chain cleavage, so-called β -scission followed by photon emission. CL technique measures the amount of photons emitted. This generates information about decomposition reactions in the drying film.

Several studies have shown, that RTIR spectroscopy is a powerful technique to monitor the drying of unsaturated fatty acid structures (Hartshorn, 1982; Mallegol et al., 1999). The absorption bands in the infrared spectra represent different structural parts in the drying oil. Time-resolved spectras give information of chemical changes during the initial oxidation process (Fig. 2).

Absorption bands relevant to the oxidation process can be monitored as a function of time following their intensity changes. The studies with real-time IR spectroscopy (RTIR) can be performed either by measuring the IR absorption through an entire film in transmission or as single reflection attenuated total reflection (ATR) measurements on the surface of the 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 (Fig. 3).

Both IR techniques present limits to be considered when evaluating the data (Mallegol et al., 1999). Reactions in a thin and outermost layer can be rather large and still not detected in transmission mode. The result of the transmission measurements gives an average absorption through the whole film. A thick film will then give very little information about the drying at the surface. 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.

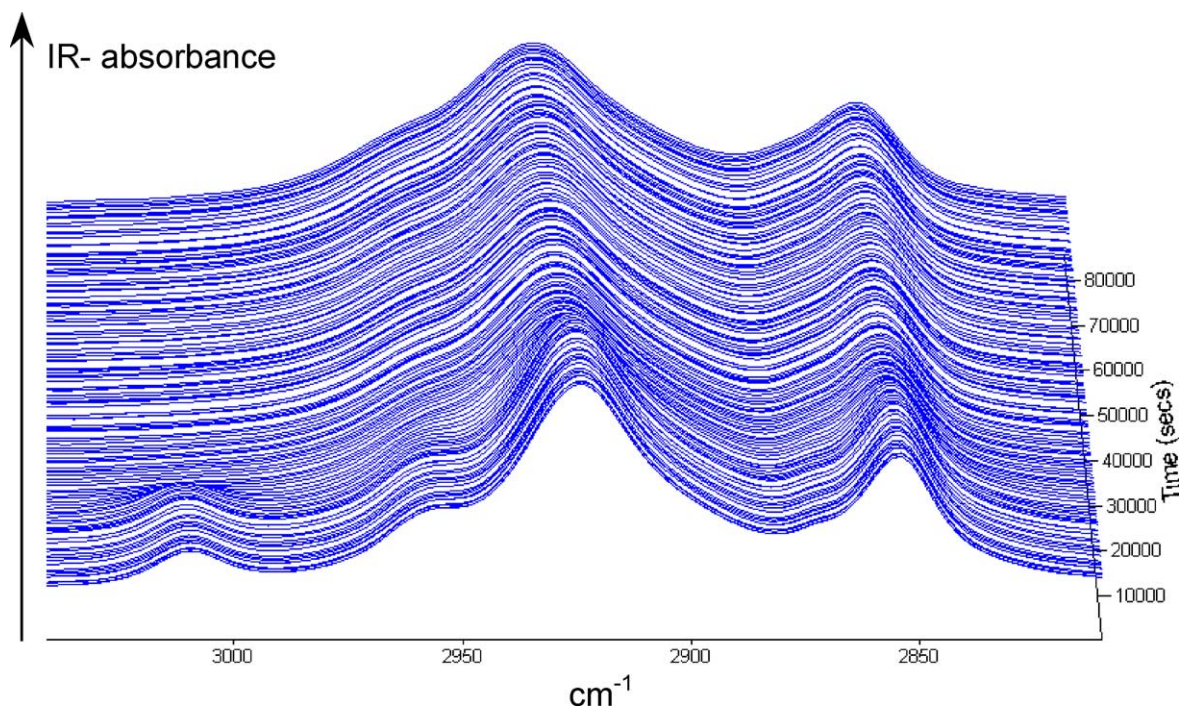


Fig. 2. Detail from a time resolved infrared spectra of oil **1**. Changes in the absorption band at 3010 cm^{-1} related to unconjugated *cis*-unsaturation as a function of time are well shown here.

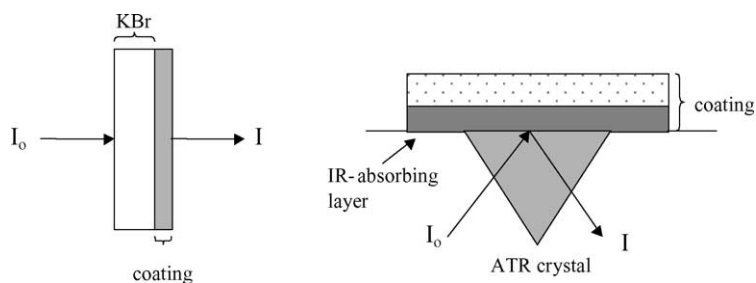


Fig. 3. Transmission measurement through the entire film vs. single reflection transmission measurements with an ATR crystal set-up.

In the present study, we have chosen to employ the ATR technique.

The present work aims to compare the drying of two different linseed oils, a conventional linseed oil (with a high percentage of linolenic acid) and an edible linseed oil (with a high percentage of linoleic acid), by a combination of RTIR and CL. The combination of these analytical techniques will give new information on the relation between structural differences and cur-

ing performance of an oxidatively drying coating film.

2. Experimental

2.1. Materials

Oils from two different varieties of linseed (*Linum usitatissimum* L.) were obtained by cold crushing of the seeds followed by refining of the raw oil with

Table 1
The fatty acid content (%) of linseed oils **1** and **2**

Fatty acid	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1
Linseed oil 1	6.0	0.1	3.3	13.0	74.2	2.7	0.1	0.4
Linseed oil 2	5.1	0.1	3.5	13.4	16.8	60.4	0.1	0.4

The oils mainly differ in the content of the reactive fatty acids linoleic (C18:2) and linolenic (C18:3).

bleach earth. Seeds were sown and harvested in Sweden during 1999. The oils were prepared, analysed and supplied by Svenska Lantmännen AB (Sweden). Both oils had very low concentrations of free fatty acid (<1 mg KOH/g) and phospholipids ($P < 1$ ppm). Oil **1** (Purolin™) originates from an edible variety of linseed and has a large content of linoleic acid (C18:2). Oil **2** originates from a traditional variety of linseed and has a large content in linolenic acid (C18:3). The fatty acid patterns of the two different oils are presented in Table 1. Co-2-ethyl-hexanoate, Hex-Cem Co-10 (10% Cobalt) from OMG Europe (Dusseldorf, Germany), has been used as the drier. The drier content was 0.1% Co when used.

2.2. Instruments and procedures

2.2.1. Real time infrared (RTIR) spectroscopy measurements

The RTIR experiments have been performed on a Perkin-Elmer Spectrum 2000 FTIR equipped with a heat controlled single reflection attenuated total reflection (ATR) accessory from Specac Ltd. (Kent,

England). TimeBase software was used to perform time-resolved measurements. The heat controlled ATR-device was set to 30, 70 or 100 °C. A small drop of oil (approximately 5 μ l) was then placed on the open-air crystal and the measurements started. The programme was set to collect a spectrum every 5 or 10 min depending on the total length of the measurements. The total length of the measurements was varied from 3–24 h depending on the temperature during the experiments. Details on the different experiments performed are listed in Table 2.

The information on the bottom layer is important when investigating the through drying properties following the disappearance of residual unsaturations in the drying coating. A droplet, approximately 5 μ l was applied to form a thin film of ~ 60 μ m on the ATR crystal. The geometrical form of the application area limits the sample volume.

The absorption bands selected for the study are summarised in Table 3 (Socrates, 2001). These wave numbers were selected based on previously reported RTIR measurements of the oxidation of methyl linoleate (Samuelsson and Johansson, 2002).

2.2.2. Chemiluminescence (CL) measurements

The CL measurements were performed on an apparatus built by Färnert Digitalteknik (Stockholm, Sweden). Inside a vacuum chamber (to ensure an accu-

Table 2
Experimental details

Experiment no.	Oil type	Drier content (% Co metal)	Temperature (°C)
1	1	0.1	30
2	1	0.1	70
3	1	0.1	100
4	1	0	70
5	1	0	100
6	2	0.1	30
7	2	0.1	70
8	2	0.1	100
9	2	0	70
10	2	0	100

All experiments were performed both with RTIR and CL measurements. Oil **1** is rich in linoleic acid; oil **2** is a traditional linseed oil (rich in linolenic acid).

Table 3
Summary of Infrared spectroscopy absorption bands used in this study

Band position (cm^{-1})	Intensity	Assignment
3010	m	$\nu(\text{C-H}) = \text{CH}$ unconjugated <i>cis</i> -unsaturation
990	s	$\nu = \text{C-H}$ bond conjugated <i>trans</i> isomers
970	m	<i>trans</i> -alkene bonds
720	s	C-H def vib <i>cis</i> -unsaturation

rate environment) a test chamber is placed to hold the sample. The holder is a temperature controlled cylinder-shaped oven of approximately 10 cm³. Gas with controlled flow can be led through the test chamber to obtain a controlled atmosphere. A quartz lid on the top of the test chamber allows emitted photons to be detected by a Hamamatsu H6180-01 integrated photon-counting head.

The test chamber temperature was set either to 30, 70 or 100 °C. A droplet sample, 20 µl, was then placed on an aluminium pan (diameter 20 mm) and inserted in the sample holder. When vacuum was reached around the test chamber, the measurements were started. A flow of air, 60 ml/min, was let through the test chamber during the entire experiment. Data were collected once a minute.

3. Results and discussion

When using linseed oil in coating applications, it is desirable to minimise negative properties such as yellowing, wrinkling of the surface and degradation of the dried films. The influence of reaction temperature and metal salt catalysts, i.e. driers on the reaction rate and the reaction path are important to understand the overall drying process of the oils.

The structural differences between linoleate and linolenate suggest that oils with a higher fraction of linolenic acid oxidise (dry) more rapidly, could be crosslinked more densely and give harder films. But it would also contain larger amounts of residual double bonds compared with the oils based on linoleic acid. Negative macroscopic effects such as skin formation, yellowing and film degradation may then appear.

Skin formation is a phenomenon that depends on several factors such as reaction rate, oxygen diffusion rate, drying temperature etc. The presence of an oxygen gradient throughout the film affects the oxidation process. More rapid drying on and near the surface of the film will result in skin formation. If the drying gives a dense polymer network, it acts as a diffusion barrier for air. Further, oxidation of the interior will be delayed leaving the oil wet and non reacted below the dried surface. Due to volumetric changes upon drying, the surface becomes wrinkled. If the resulting surface network is less dense or if the oxidation rate is slower, the influence of such diffusion barrier will

be less apparent.

Yellowing is another macroscopic negative effect. It depends mainly on residual conjugated double bonds, which also affect the long-term stability of the film. The coloured components absorb UV light and subsequently disappear in sunlight.

The oxidation is normally accelerated by the addition of a drier, an organic metal salt which catalyses the decomposition of hydroperoxides via a redox mechanism (Mallegol et al., 2000). This will increase the radical concentration in the system at an early stage and increase the overall drying rate. An increased radical concentration will also affect the relative rates of the different decomposition reactions with consequences on ratio of chain scission/addition products.

The reaction of addition (addition to double bonds) dominates at early stages since reactive conjugated dienes are present at this stage. These addition reactions do not cause any chemiluminescence. The CL signal is related to only a part of the oxidation process where decomposition reactions generate excited carbonyls, which eventually will relax and, to some quantum yield, emit photons. A previous study, on the uncatalysed oxidation of pure methyl linoleate suggests that the CL signal does not appear in the very early stages of the oxidation but when β -scission starts (Blakey and George, 2001; Samuelsson and Johansson, 2002). It has been shown that almost all unconjugated *cis*-double bonds (3010 cm⁻¹) in methyl linoleate can be consumed in the auto-oxidation cycle, (Fig. 4), before the chemiluminescence commences. In comparison with the RTIR analysis there are some major differences. The ATR technique used in the RTIR analysis does not follow the entire film. Only the bottom layer of the test sample is analysed, which can be associated with through drying of the film. In CL analysis the signal results from measuring the entire test sample but only a part of the oxidation process. The effect of the airflow on CL measurements has been evaluated in the region 10–120 ml/min and the oxidation rate is shown to be independent in this region (Samuelsson and Johansson, 2002).

3.1. Effect of the temperature on the drying process

Oil 1, containing mainly linoleate esters, follows an expected dependency with temperature for the uncatalysed system. The oxidation reaction is acceler-

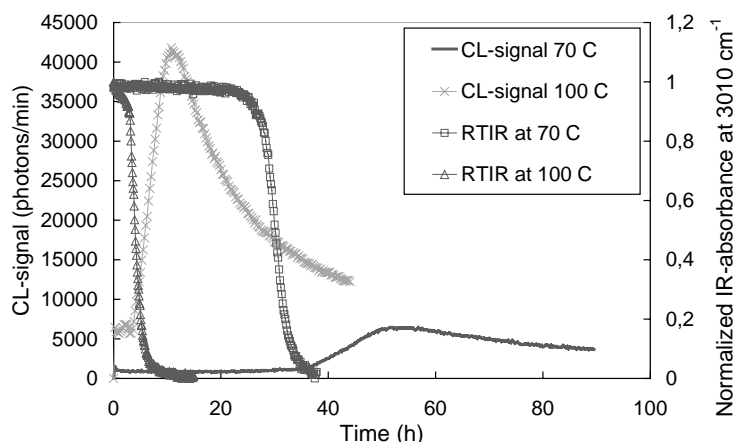


Fig. 4. CL-signal and the change of absorption at 3010 cm^{-1} (RTIR) with time for oil **1** (C18:2) at 70 and 100°C (experiments 4 and 5, Table 2). In both experiments, it can be observed that photon emissions start when the isolated *cis* double bonds are consumed.

ated with increased temperature. RTIR measurements shows a shorter induction time for the drying of the films at higher temperatures and, also shows a low amount of residual unsaturations in the test samples at all temperatures (see Fig. 4). The dried films show no tendency towards skin formation and wrinkling. This indicates that the auto-oxidation is only accelerated with raised temperature and that no diffusion barriers are formed. The complete disappearance of the unconjugated *cis*-unsaturations before the CL signal commences suggests that the first stage of the oxidation mainly leads to crosslinking rather than chain scis-

sion. Furthermore, the formation of conjugated *trans* double bonds (RTIR, 990 cm^{-1}) appears when the *cis*-unsaturation (RTIR, 3010 cm^{-1}) disappears. The conjugated *trans* double bonds are then consumed according to Fig. 1, mainly leaving isolated double bonds (RTIR, $970, 720\text{ cm}^{-1}$). Raised temperature generates a stronger CL signal but also a fast decrease of the signal. The film dries faster.

For oil **2**, having a large content of linolenic acid, an increased temperature for the uncatalysed oxidation results in an increased rate and stronger CL signal in the same way as for oil **1**, though the onset of oxidation is much more rapid and proceeds at a higher rate than oil **1** (Fig. 5). No tendency to skin formation and wrinkling is seen.

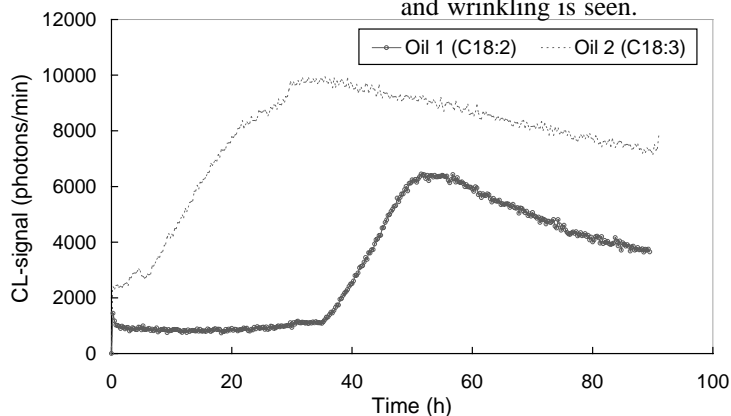


Fig. 5. CL signal at 70°C for oil **1** (C18:2) and oil **2** (C18:3) (experiments 4 and 9, Table 2). Photon emissions (chain-scission) for the former oil start after a lag period of ca 35 h.

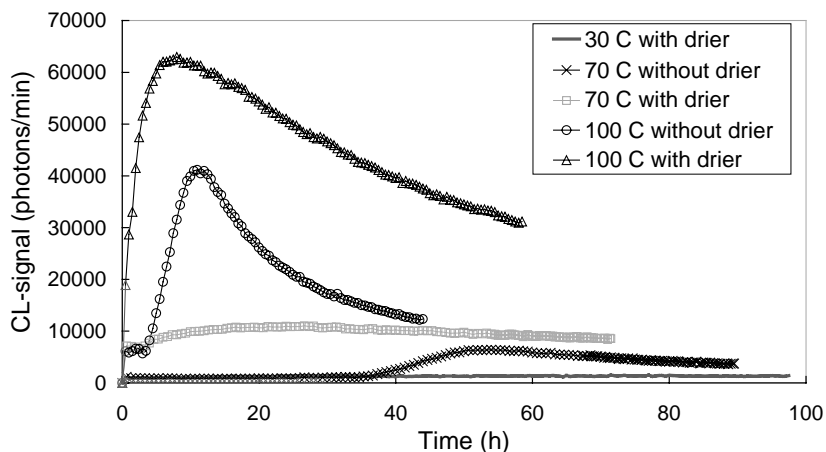


Fig. 6. CL signal as function of time for oil 1 (C18:2) with and/or without drier at 30, 70 and 100°C experiment.

3.2. Effect of the drier on the oxidative drying process

The addition of the Cobalt octanoate drier to the two oils shows significantly different results.

For oil 1 (C18:2) the CL signal becomes stronger and also starts earlier, see Fig. 6. This indicates that the increased concentration of radicals formed using a drier, increases the overall reaction rate and the possibility for chain scission to some extent.

For oil 1, the residual amount of unconjugated *cis*-unsaturations is low in all cases suggesting a good long-term stability, see Fig. 7. The films of these rapidly cured samples of oil 1 show some wrinkles indicating a slightly too fast surface curing generating

a sparse network not dense enough to inhibit diffusion of air below the surface. The wrinkling is significantly less compared to films based on oil 2 (C18:3) cured at the same conditions.

For oil 2, the addition of a drier increases the initial drying rate significantly minimising the induction time of the auto-oxidation. The absorption at 3010 cm^{-1} decreases faster at higher temperatures but also results in higher amounts of residual unconjugated *cis*-unsaturations (see Fig. 8).

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 content at the bottom of the film. When

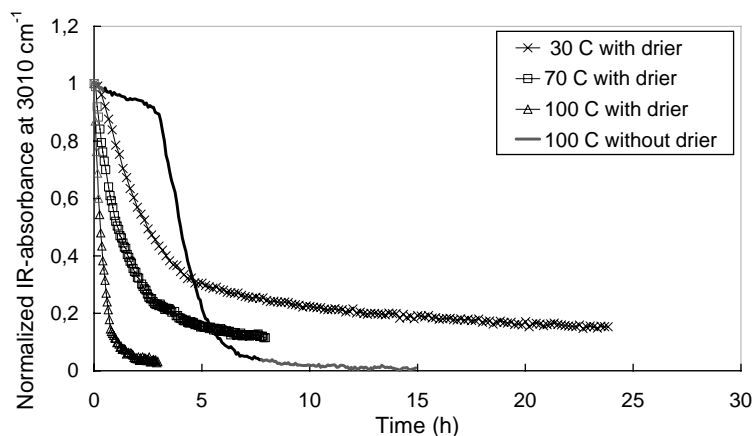


Fig. 7. Change of absorption at 3010 cm^{-1} (RTIR) with time for oil 1 (C18:2) for experiment 1, 2, 3, and 5 (see Table 2).

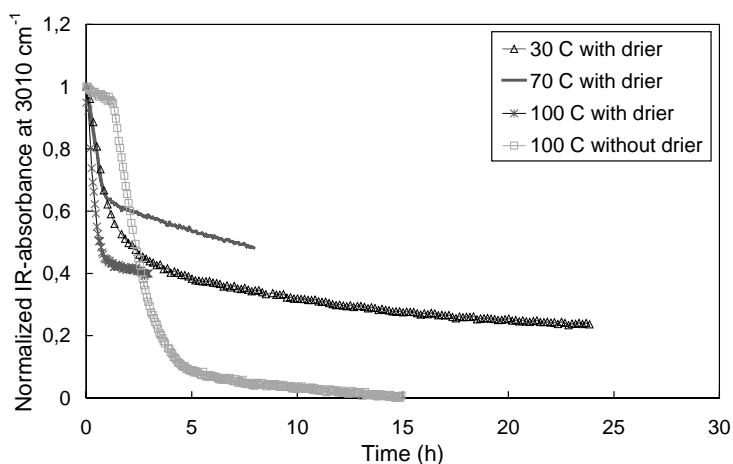


Fig. 8. Change of absorption at 3010 cm^{-1} (RTIR) with time for oil **2** (C18:3) for experiment 6, 7, 8 and 9 (see Table 2).

comparing experiments 6, 7, and 8 it is seen that the lowest temperature ($30\text{ }^{\circ}\text{C}$) result in the lowest amount of residual unsaturations in the bottom layer. Increasing the temperature to $70\text{ }^{\circ}\text{C}$ result in higher initial rate 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 result in an abrupt stop but at a lower level of residual unsaturations. This lower level may be due to the fact that the higher temperature makes the film softer which reduces the barrier function of the “skin”.

Comparing the CL results for oil **2** supports this theory (see Fig. 9). 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 **1** (experiments 1–5) and suggests that the oxidation reactions are limited by barrier (skin) formation.

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

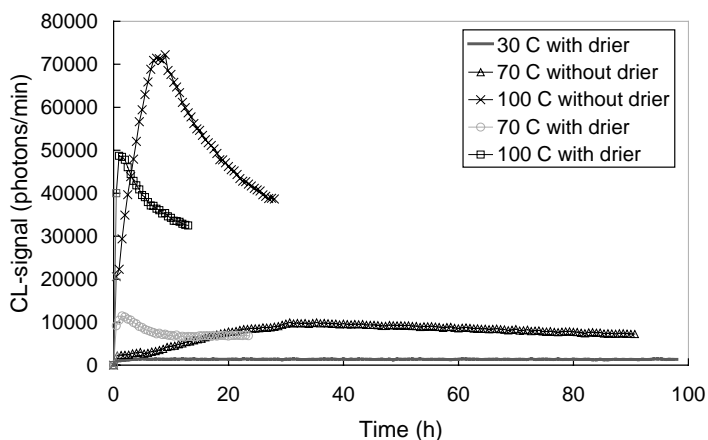


Fig. 9. CL signal as function of time for oil **2** (C18:3) experiments 6, 7, 8, 9 and 10.

4. Conclusions

The present work shows, that large difference in the curing performance of linseed oil coatings can be obtained by changing the fatty acid pattern in the oils. Traditional linseed oil, rich in linolenic acid, dries rapid but the coating suffers from high degrees of residual unsaturation in the cured film. This is detrimental for the long-term durability and colourfastness. Too rapid drying will also result in poor through cure due the formation of a skin layer acting as a diffusion barrier to oxygen. A linseed oil variety rich in linoleic acid is shown to exhibit a very different behaviour. This oil will produce slightly softer films but with a significantly lower amount of residual unsaturation, no problem with skin formation, and good through cure. This will result, in a coating with much better durability and less problem with yellowing. Two different techniques, chemiluminescence and real-time infrared spectroscopy, in combination are shown to be versatile tools to study the drying performance of oxidatively drying coating systems.

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