Graphical Abstract

Without PbO

PbO 5%

At air

The drying of linseed oil investigated by Fourier transform infrared spectroscopy: historical recipes and influence of lead compounds

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Abstract

*Lead compounds have been commonly used since the Renaissance period to increase the drying properties of oils. This article presents new insights on the mechanisms involved: Fourier Transform Infrared Spectroscopy (FT-IR) has been used to investigate the effects of lead oxide on the drying process of linseed oil. The changes occurring during the drying of oil and the influence generated by the use of PbO were monitored by integrating absorption bands of interest such as the $\nu(\text{O-H})$ absorption band at 3500 cm^{-1} , and the $\nu(\text{C-H})$ in *cis* $\text{C}=\text{C-H}$ band at 3010 cm^{-1} . Results indicate that the addition of lead oxide accelerates the drying process and reduces the induction time (4 times with 5% PbO), without causing major changes in the mechanisms involved. An optimal amount of 5 % PbO was determined, as compared to 1 and 20 %. Historical recipes have been reviewed and the effect of specific oil preparation parameters such as the heating of oil while adding PbO addition and the addition of water have been investigated.*

Keywords: oil paint, drier, litharge, Attenuated Total Reflection –Fourier Transform Infrared, oxidative polymerization

1. Introduction

Oils used in historical paintings are natural drying oils, such as linseed, walnut or poppy seed oils. Their main components are triglycerides, which are esters of a mixture of saturated and polyunsaturated fatty acids responsible for air-drying properties [1]. The drying of linseed oil is a chemical process taking place spontaneously when exposed to the air, generally considered to be due to a process of autoxidation followed by polymerization [1-8]. It is a multi-step reaction, starting with the autoxidation of C=C bonds of the fatty acids chain into peroxidic compounds via an allyl stabilized radical. After an induction period attributed to the presence of natural antioxidants [2], the oil absorbs large amounts of oxygen. In the meantime, non-conjugated double bonds are converted into conjugated double bonds [5]. The reversible O₂ addition facilitates isomerization of the unconjugated *cis-cis* bonds to successively more thermodynamically favourable conjugated *cis-trans* and *trans-trans* peroxy radicals [1, 4]. The following cleavage of unstable peroxides and hydroperoxides lead to the formation of radical species, and to their recombination and/ or to their fragmentation into smaller alcohols and aldehydes [3]. In the sequence, the hydroperoxides undergo a polymerization process following initiation, propagation and termination reactions [7-9]. This autoxidative crosslinking process is responsible for the formation of a solid film observed over time. The molecular weight grows mostly during the polymerization step where C–C, C–O–C and C–O–O–C bonds are formed through the direct reaction between free radicals issued from the hydroperoxide decomposition [7]. The propagation of the polymerization can also proceed through a hydrogen abstraction mechanism producing allylic radicals, or by addition of the ROO• radical to conjugated double bonds. After the addition reaction, the radicals allow polymerization to follow, leading to epoxy and peroxide moieties. Although a film of linseed oil is touch-dry in a few days, the drying reactions continue for many years and, as cross-linking proceeds, a progressive hardening occurs, moderated by the presence of unchanged glycerides [2, 10].

To fasten the curing process, the use of metallic driers appeared to have yielded successful results, for which it became a common practice among painters that remains up to date. By definition, “a drier for paint (...) will induce or speed up the setting or drying or solidification of a liquid oil film” [11]. Nowadays driers are typically metal soaps of either alkaline-earth metals or heavy metals [9, 12]. Unlike most catalysts, driers can catalyse more than one chemical reaction in the autoxidative process. Driers can increase the O₂ uptake, reduce the induction time, and promote peroxide decomposition [11, 13]. Different classifications of driers exist in the paint industry [9, 14]. The historical one was based on their function namely i) surface drier, ii) through drier and iii) auxiliary drier [9, 15]. “Surface driers” are based on multivalent metals and as a consequence can undergo facile and reversible changes in oxidation states, which can promote the autoxidative curing process. They are also known to dry from the top down. “Through driers” promote curing beneath the surface of the coating. “Auxiliary driers” inhibit phase separation of the surface from the polymeric phase. Both cobalt and manganese-based driers can easily dry the surface of a produced film but leave the subsurface soft. Lead-based driers have the beneficial effect of more uniform drying throughout the entire film thickness, thus leading to films that have a good balance of hardness, toughness, flexibility and chemical resistance [9]. Another classification, that is most common nowadays, divides driers in two categories: those that affect the oxidation of oils, (which can be surface driers or through driers); and those that affect the polymerization process itself, called secondary or sometimes auxiliary driers and which are often compounds containing metals with only one possible oxidation state (zinc, calcium, potassium, lithium, sodium compounds) [7, 8, 12]. Lead compounds can be considered as both oxidizing driers and as polymerization-affecting driers [13].

Litharge (PbO) is historically the most commonly used lead compound [16, 17]. When litharge is mixed to oil, it provokes the saponification of some triglycerides and the formation

of lead soaps [18]. At the end of the 19th century the paint industry started introducing soluble metal soaps directly (manganese and lead linoleates and resinates), instead of generating them *in-situ* [17]. At the beginning of the 20th century, the efficiency of cobalt soaps made them very popular. Due to toxicological and environmental concerns, lead driers were phased out in the mid to late 20th century and were replaced by other through driers such as cobalt or zirconium-based ones [7, 13, 19].

In the context of an important industrial impact, the siccative action of cobalt-based driers has been widely studied. Mallegol *et al.* [14] have shown that oxidative polymerisation mechanism of drying oils, with or without surface drier, is the same. They investigated the drying of films in the presence of cobalt drier, revealing changes in kinetics but not in stoichiometry of reactions. These changes can be explained by peroxide decomposition induced by cobalt. Conversely, while they have probably been the first and most used driers since the Antiquity, the drying actions and properties of lead-based compounds have not been investigated as thoroughly as modern (20th Century) driers. Tumosa and Mecklenburg [13] recalls that painters have used lead for a long time to improve their oil properties, but its action has not always been recognised by all chemists: in 1941, Bennett commented on the effect of lead driers: ‘By itself lead is not a powerful drying accelerator, at least for simple oil systems, and it does not appreciably alter the course of oxidation of the oil’.

In the present work, we have been investigating numerous historical recipes, in order to identify the most standard oil preparation method, which we used to prepare mock-up samples. As detailed below, lead can be introduced in oil under different forms, with different additional ingredients and under different temperature conditions. Among these recipes, mixing and heating oil with litharge was found to be the most common process. The short term effects of various lead compounds (in particular litharge) on oil in the synthesis of lead media (in cosmetics and paintings) have been previously studied by means of FTIR study [18,

20]. In particular, the saponification process induced by lead compounds on oil triglycerides was monitored over a few hours. In the present paper, we aim to understand the way lead oxide added to linseed oil acts on the drying process. We follow the evolution during eight months of the FTIR spectra of PbO/oil mixtures, prepared in various conditions. The influence of PbO concentration and of the oil preparation method is investigated by means of ATR-FTIR. As a comparison, PbCO₃ was also tested as a drier, at one specific concentration. To fully interpret our results, an extensive survey of the existing literature on the drying of linseed oil and its FTIR bands assignments has been done and presented.

2. Experimental

2.1. Historical sources and reconstitutions

We can see from historical sources from the 12th Century until now that the methods of refining and processing oils have not changed dramatically over centuries. One of the first recipes, from Eraclius (12th Century), advises to prepare the oil “for tempering colours” by boiling oil with lime, then adding ceruse and placing the mixture in the sun [21]. The addition of a lead compound in the preparation of drying oils has been commonly used since then. The main driers at the end of the Renaissance period are litharge, lead white, red lead (minium (Pb₃O₄)) and sulfate of zinc (ZnSO₄). Litharge was available in two varieties: silver and gold. The so-called silver litharge (yellow colour) was heated at higher temperature and reported to be a harder material than the gold litharge with a red colour [17]. The silver one was recommended over the gold one because it was more highly oxidized and would therefore make a more effective drier [17]. Lead white is composed of different proportions of cerussite (PbCO₃) and hydrocerussite (2PbCO₃, Pb(OH)₂) [22]; it is frequently referred as *ceruse* in the manuscripts.

129 We decided to focus our study particularly on the manuscript written by Turquet de Mayerne
130 (1573-1654), an experimental Swiss chemist and friend of artists. This is an easily accessible
131 manuscript compiling great knowledge about the preparation of colours, supports, oils for
132 painting, gilding, ink... [23] Among 170 folios, 36 describe oil treatment and media
133 preparation, underlying here the importance of such process. Folios can describe several
134 recipes, a total of 58 recipes for oils have been found with more or less detailed which could
135 include a simple note about the preferred use of siccative oil and/or the complete recipe of oil
136 preparation process. Some recipes (folios 94 and 143) indicate one or several « washing
137 steps » with water. For example, in folio 94, the oil is first filtered through sand and then
138 added to water. The filtration or addition of sand would help the oil purification by removing
139 plant mucilage. Further treatments aim to whiten the oil and / or making it more siccative. To
140 lighten the oil, it is usually recommended to place it in the sun. As a secondary effect, oil
141 placed in direct sunlight with periodic stirring, thickens. That is why it is sometimes
142 suggested to carry out the bleaching process at a time of the year when the sun is not too
143 strong, as in March (folio 94, 93), to prevent a too strong thickening. On the contrary, other
144 recipes advice to expose the oil to the sun during warm weather, as the thickening is
145 associated to an increase of the oil siccativity. Another method of bodying the oil is to heat it.
146 Various « ingredients » can be added during heating or simple bleaching process, mainly
147 siccative materials. The most common are the lead compounds and the 29 recipes mentioning
148 the use of lead compounds in the Turquet de Mayerne manuscript are listed in Table 1.
149 *Litharge* is the most cited (25 recipes), with *lead white* present in 11 recipes and *ceruse* in one
150 recipe. It is probable that *ceruse* designates here the white lead-based pigment without
151 distinction of composition. The terms *litharge* or *litharge of gold* are almost equally used and
152 we cannot state whether this distinction is made purposely or not. One recipe (folio 135)
153 recommended that lead white should be mixed with oil, together with bread (« *made into*

154 *crummes*») and sawdust, placed in the sun for four or five days, stirring the ingredients
155 together five or six times a day. Bread might be added to absorb the water from oil: 7 recipes
156 mention it (4 with white bread and 3 with crust of bread) and sawdust would absorb any
157 remaining plant mucilage and lecithin [24]. Four recipes indicate the use of minium/mine
158 (Pb_3O_4) and three recipes mention the use of a pot / container made with lead. Other
159 « ingredients » are suggested, some known to be siccative, such as ZnSO_4 (mentioned as
160 « *couperose blanche* »). Saponifiers are also added, which neutralize free fatty acids, for
161 example, quick lime (calcium oxide) or ashes from wood containing KOH. For some, whether
162 they are siccative or not is not assessed: it is advised for example to add powdered glass as a
163 drier (folio 20). It gives good handling properties but its influence on drying time is still under
164 discussion [25]. Alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$) might also be added to water before the bleaching
165 process and according to Kirby and White [24] the addition of alum to water might produce a
166 weakly acidic solution, which would coagulate suspended mucilaginous material. The
167 addition of vinegar (folios 137 and 139) before bleaching or heating treatments might have
168 the same effect. More unexpected compounds have also been found, such as urine of man
169 (folio 145), brandy (folio 140), and even onions and garlic (both folio 90). The use of garlic is
170 common to lighten the oil and supply water during the heating process [24], but it is not
171 completely understood. Even the known siccative compounds such as litharge and ceruse are
172 only poorly documented and the mechanisms involved are not fully detailed in the literature.
173 For our reconstructions, litharge was chosen since it is the most commonly used siccative
174 (Table 1). Despite minor differences in the proportions or additional ingredients, the treatment
175 process reported to prepare siccative oil with litharge is generally the same. The mass
176 proportions of litharge in oil vary from 1 to 20 % in most of the recipes [26]. Depending on
177 the proportions, the resulted medium can be either added in a small quantity to already
178 prepared colors, or mixed to pigments or resins to prepare paint or varnish (leading to final

179 lead proportions much lower). Caution was generally taken not to heat the oil too strongly,
 180 which would deepen the color; gentle heat for roughly an hour is often recommended. Some
 181 recipes also recommend adding water before and/or during heating the oil with lead oxide (3
 182 recipes in Table 1). This limits the temperature, increases the saponification process and
 183 prevents the medium from darkening [20, 26]. According to Maroger [27], the oil obtained is
 184 “far superior as a medium for painting”, and he even attributed this new process to Leonardo
 185 da Vinci as it improves greatly the final oil properties.

186

187 Table 1: Recipes from Turquet de Mayerne’s manuscript, mentioning the introduction of a
 188 lead compounds in oil preparations. *: undefined in the recipe

189

Folio	Ingredients	Proportion (weight?)	Process	Expected result
6	Oil, litharge	*	On fire ½ h -1h	“to make black colours dry”
7	Oil, lead white	*	Under the sun light	to whiten
7	Oil, litharge or ceruse	*	Under the sun light	« best varnish » water resistant – siccative oil
11	Oil, litharge	*	*	“siccative oil (for <i>imprimatura</i>)”
16	Nut oil litharge of gold minium	1 1/32 1/64	Gentle heat (boil for 1h), then under the sun light	“for Oil white and clear as water”
17	Oil, Litharge of gold	1 1/12	Gentle heat, boil for 2h	*
18	Linseed oil, Litharge of gold, aspic oil	1 1/6 *	Gentle heat (boil for 1h), Continuous stirring	“waterproof Oils, to varnish old paintings”
19	Oil, litharge	1 1/4 to 1/3	*	“drying of black colours”
19	Nut oil, lead white	*	Sun, in a lead-container	“oil whitened and thickened”
20	Oil, litharge / mine / lead white	<i>a lot</i>	Gentle heat (long time)	
28	Nut Oil litharge of gold Hot water	1 1/4	Gentle heat	“to varnish wood and iron/ to prepare canvas”
31	linseed Oil litharge of gold + resins	1 1/8	heat Under the sun light	“siccative varnish (for wood)”
32	Oil, litharge	*	boiling	“oil drying in half a day”
46	Varnish, litharge of gold (little)	*	*	“to make varnish dry”
48	Oil (nut/ linseed), Litharge / or nothing	*	heat / or under the sun light	“very siccative amber varnish”
50	Oil Lead white Litharge of gold, Umber	1 3/4 1/4 1/2	boil for 3h	“oil for varnish”

90	Linseed Oil, garlic, lead white, white onion	*	heat (1/4h)	“oil for gold paint”
93	Linseed Oil, Litharge, mine	*	Gentle heat until boiling, then sun of March	“siccative Oil”
95	Oil, litharge, Silberglette, « spalte » (bitumen)	*	heat until boiling	“oil siccative (for shadows, to be used in glazes)”
96	Oil (nut/linseed), litharge of gold: silberglette	*	heat (until boiling), to repeat again 5 or 6 times.	“for dark colours (1 - 2 drops added to the paint)”
112	Poppy Oil, litharge/ lead white	*	« infusion »	“oil for white, azure”
139	Purified Linseed Oil, lead white, rye bread	*	Sun 8 -10 days	“clear oil”
139	Oil Litharge of gold white vinegar	1 1/3 1	Stirring each day	*
140	Oil, crust bread	*	In a lead container, in the shade	“until whitening”
142	linseed/ nut/ poppy Oil litharge of gold Water	1 1/6 2	In boiling oil, add litharge, stirring for 7.5 min, then add water and boil for 1 to 2h	“White oil that do not thicken, is clear and dries”
143	linseed/ nut Oil (hot) litharge		heat, mix « long enough », settle 15-20days	“litharge oil clear and white. Very siccative”
145	nut Oil water litharge of gold	1 1 1/6	Gentle heat, mix, Boil 1/2h	“siccative litharge oil”
146	Oil, lead white	*	heat, mix 1h (without boiling)	“white oil”
162-163	Linseed Oil Litharge	1 1/8	Gentle heat (4h), settle, then strong fire in an iron pot	“highly siccative oil. To varnish on wood”.

190

191 2.2. Preparation of films

192 Linseed oil was purchased from Laverdure, Paris (cat. A.). Conditions and names are
193 summarized in Table 2.

194 *Heated oil (H)*

195 Oil was heated in a beaker at 150°C for 2h under magnetic stirring.

196 *Oil with litharge, heating process (HL_x)*

197 Oils were prepared with various amounts of litharge, from Interchim (Montlucon, France), to
198 study the influence of lead oxide content on the film drying: x= 1, 5 and 20 % of PbO (in
199 weight). Litharge and raw linseed oil are first mixed thoroughly by grinding the litharge in the
200 oil at room temperature. The litharge is first added to a little quantity of oil (few droplets) and
201 ground in a mortar. The rest of oil is then added to the mixture, mixed and put in a beaker

202 where the preparation is heated at 150 °C for 2h under continuous magnetic stirring.

203 *Oil with litharge and addition of water, heating process (HLw_5)*

204 Oils heated with litharge in presence of water were also prepared. Our reconstructions were
205 prepared by heating a mixture of water, oil, and litharge (in a single mass ratio of 5%). The
206 litharge is first added to a little quantity of oil (few droplets) to be ground in a mortar. The rest
207 of oil is then added to the mixture, mixed thoroughly and placed in a beaker to which water is
208 added, where the initial water content is half the weight of oil. Finally, the preparation is
209 heated at 100 °C for 2h under continuous magnetic stirring. In order to always have water in
210 the sample during the heating process, water was added at regular time intervals (every 15
211 min). The total weight of water introduced equals the quantity of oil. After heating, the
212 aqueous phase was separated by settling.

213 *Heated oil with litharge added at room temperature (HL_amb_x)*

214 As a comparison, lead oxide was also added to heated oil(H), in the same ratios used for the
215 HL conditions (x=1, 5, 20). Litharge and heated linseed oil were mixed thoroughly by grinding
216 the litharge in the oil.

217 *Oil with PbCO₃ at room temperature (HC_amb_1)*

218 Finally, PbCO₃ (from Alfa (Aesar), ACS) was also added to heated oil, in 1 % in weight, and
219 ground in it in the same way as previously described.

220 *Preparation of films and drying conditions*

221 The different oils were then uniformly spread in the next hour (particularly for the ‘D’
222 samples, to avoid sedimentation) on glass slides in 30 µm-thick films using an *Erichsen 320*
223 film applicator. The slides were kept under laboratory conditions, in a normally illuminated
224 area (with day and night cycles) and at room temperature simply sheltered from dust.

225 It has to be establish here that fresh linseed oil films have not been studied under the same
226 conditions: the obtained films were not sufficiently homogeneous, as applied on glass plates

without specific chemical preparation, to have reproducible properties. Since all the prepared oils are based on linseed oil heated 2h at 150°C, “H” used as the reference sample, instead of fresh oil.

Table 2: Oil codes

Oil code	Preparation process
H	Linseed oil heated 2h at 150°C
HL_x	Linseed oil + PbO x% heated 2h at 150°C x=1, 5, 20
HLw_5	Linseed oil + PbO 5% heated 2h at 150°C with water
HL_amb_x	Heated linseed oil + PbO x% (added at ambient T°C) x=1, 5, 20
HC_amb_1	Heated linseed oil + PbCO ₃ 1% (added at ambient T°C)

2.3. FTIR spectroscopy

ATR/FT-IR was chosen to follow changes in the chemical composition during the film drying. It does not require any chemical preparation. FTIR spectra were recorded at room temperature with a Cary 630 Agilent spectrometer using the ATR accessory. At regular time, a sample was taken from the drying films by scratching the film. The sample was then placed on top of the ATR crystal. For liquid samples, no pressure was applied while solid samples required a closer contact between the sample and the ATR crystal, which was supplied by applying supplementary pressure on the sample. With this method of sampling, the measurements are done using the entire thickness of the film (30µm), without specific selectivity to the outermost surface. For each measurement, three spectra of the same film were recorded to assess the reproducibility, as an accumulation of 32 scans, with a spectral resolution of 4 cm⁻¹. Each drying experiment has been done twice (two films have been investigated for each condition). The reactions were monitored by FTIR over a total of 500 h and a final spectrum was recorded after 8 months. During the first day, a spectrum was recorded every hour. Since the changes observed in the FTIR spectra over time during the drying of oil occurred much slower after 24 h, the samples were then monitored twice every day during the first week and ultimately, once a day until 500 h were reached. The software MicrolabPC was used to record

the spectra that were then processed with PyMca software to evaluate the bands area [28]. The evolution of the main bands have been calculated by integrating the spectral intensity over specific regions of interest (ROI), detailed below in Table 3, using the PyMca ROI imaging tool. In order to better highlight slight modifications, the first spectrum of each set was subtracted first and the ROI were measured on the subtracted spectra, yielding the absorbance spectrum given by $[A(t) - A(t=0)] = -\log(I_t / I_{t=0})$ [29]. The integration values of new peaks or peaks increasing during drying are then positive; they are conversely negative for decreasing peaks.

3. Results and discussion

3.1. FTIR spectra of the heated oil system (H): Assignment of the main peaks and evolution upon drying

The variations of absorption bands in the FTIR spectrum during the drying of pure linseed oil have been previously depicted in the literature [2-7, 29-42]. We recall in Table 3 the main identified characteristic peaks in linseed oil spectrum and their main variations during drying, according to the literature and to our measurements.

Table 3: Left: assignment of the main absorption bands observed in the oils spectra, and their evolution during drying **according to the literature**, from ref 2-7 and 29-42. Right: the main evolutions observed during drying of sample “H” **over 8 months**. v: stretching, _{as}: antisymmetric, _s: symmetric, δ : bending, ω : wagging (all indicated when explicitly used in the publication).

Global assignment	Absorption band	Assignment	Evolution during drying, in the literature	Evolution during drying (over 8 months) for H
v(OH): hydroperoxides, alcohols and acids	3340 ³⁴ / 3430 ² / 3425 ³ / 3455 ³⁰	v(OH) ^{2,3, 30, 34}	formation and increase ³⁴ appear at 60°C, after 22h. Decrease during photolysis ³	Formation and increase, then stabilisation and slight decrease.
	3200-3600 ^{14,31} , peaked at ~3465 ⁴ / 3472 ⁷ 3541-3600 ^{5, 32} (broad)	v(OH) hydroxyl, hydroperoxides ^{4, 7, 14, 31} v(O-H) (free-bonded) hydroperoxides, alcohols and acids ^{5, 32}	Appear ⁴ formation. linseed oil: increase first then decrease. tung oil: slower, less intense ⁵	
	3512-3525 ⁴ / 3470 ³ / 3435 ³³	v(OH) alcohols ³ , secondary alcohols ⁴ , alcohols and hydrogen peroxide ³³		
	3467 ³⁴	first overtone of v(C=O) vibration ³⁴		

v (CH) unconjugated <i>cis</i> double bonds	3008 - 3011	v(CH) -CHCH=CH- unconjugated <i>cis</i> double bonds ^{3, 4, 31, 33, 35, 36}	disappearance. oxidation / conversion to <i>trans</i> (970) and conjugated (988 and 947) ⁴	Disappearance (several hours/ days)
v (CH) CH3	2956-2960	v(CH) -CHCH=CH ^{2, 34}	complete disappearance ^{2, 34}	
v(CH) CH2	2927	v(CH) CH3 ^{2, 4, 34, 35, 36}	decrease	
	2855-2853	v _a (CH) CH2 ^{2, 4, 34, 35, 36}	loss of some hydrocarbon = oxidative chain with cleavage reactions known to yield volatile oxidation products ⁴	Decrease (strongly then stabilisation)
	2810 and 2171	v _s (CH) CH2 ^{2, 4, 34, 35, 36}		
		Aldehydes ^{3, 29}	in volatile compounds (formed at 60°C) ³	Not observed
v(-OH) COOH	2600 ²	v(-OH) COOH ²	formation of a shoulder (with photoageing)	Formation
v(C=O), secondary oxidation products	1780 ³¹	v(C=O), secondary oxidation products ³¹	formation	
	1776 ^{4, 37} (1850-1750) ⁴	v (C=O) peracids, peresters, γlactones ³⁷ and anhydrides ⁴	Appear ⁴	Formation
	1750-1700	v (C=O) ketones, ester, acid carbonyl ⁴	Appear ⁴	formation
v(C=O) ester	1747-1737	v (C=O) stretching ester ^{2, 4, 33, 34, 35, 37, 38}	broadening - move from 1744 to 1740 ³⁴ - increase during oxidative polymerization ⁴ - decrease at 60°C ³ - decrease; increase in same conditions with Cu acetates ³⁸ - broadening and minor shift to lower frequency ³⁷	Broadening and shift from 1744 to 1740 cm ⁻¹
v (C=O) acids, aldehyde, ketones	1720 ^{3,5,14,28}	v (C=O) ^{5,28} in saturated ketones ^{3, 14}	broadening: formation of carbonyl-containing species such as aldehydes, ketones and carboxylic acids ^{5,28} Formation (shoulder) ⁴	
	1715 ⁴ / 1710 ^{14, 30} 1695-1720 ^{3,35} 1695 ¹⁴ 1698-1696 ^{3,31}	v (C=O) COOH ^{4, 14, 3, 35} COOH acid/ aldehyde ³⁰ unsaturated acid ¹⁴ v (C=O) α,β unsaturated ketones ^{3, 31}	Not visible ¹⁴ Increase ^{3,31}	Formation and increase
v (C=C) <i>cis</i>	1652 ^{4, 35}	v (C=C) <i>cis</i> -CH=CH- ^{4, 35}	oxidation / conversion to <i>trans</i> (970) and conjugated (988 and 947) ⁴	
	1652 ^{34, 36} / 1658-1654 ²	v (C=C) ^{2, 34, 36}	move to 1634 ³⁴ complete disappearance ²	decrease
	1670-1500	βunsaturated carbonyl ⁴		
	1640	weak <i>cis</i> C=C ³⁷	disappearance	
v(C=C) conjugated	1633 ^{2,4,31} /1624 ³⁷	v(C=C) conjugated ^{2, 4, 31, 37}	formation	formation
	1633 ³	v(C=C) conjugated with C=O ketones ³		
	1622	v(C=O) lead carboxylates ⁴	when lead white present ⁴	
v (CO) lead carboxylate	1573	v _{as} (CO) in carboxylates ³⁴	appear after several days at room temperature ³⁴	
	1537 ⁴ / 1534 ³⁹	in particular lead carboxylates ^{4, 39}	Appears in Oil + lead white / PbO after 12years ³⁹	
δ(CH) CH2, CH3	1464-1463	δ(CH) CH2, CH3 ^{2, 4, 14, 34, 35, 40}		Increase slightly
	1456 + 1452 sh	Shown, not discussed ⁴		Not observed

*	1418 ^{2,4,34}	ν (C-O) in COOH ⁴ ω (CH ₂) in -CH ₂ -CO-O- ² deformation (CH) in methylene ³⁴	formation	formation
ν (CO) lead carboxylate	1404 ³⁷ 1393 ³⁹	ν_s (CO) in carboxylates ³⁷ Lead carboxylates ³⁹	appear after several days of curing at room temperature ³⁷ Oil + litharge after 12years ³⁹	
(CH ₂)	1377 ^{2,4} / 1375 ³⁴ / 1370 ³²	Deformation CH in methyl ³⁴ ω (CH ₂) ^{2, 4, 32}		Increase
	1300	ν (C-O) secondary alcohols ⁴		
	1200-1315	ν (C-O) carboxylic acid ³	global increase between 1300-1000	
ν (C-O) in triglycerides ester linkage	1238	ν (C-O) in triglycerides ester linkage ^{2, 4, 34, 35, 36} + ν_{as} C-CO-O- ³⁴	increase during oxidative polymerization ⁴	Increase
	1100-1210	ν (C-C-O-) alcohols and hydroperoxides ³		Global increase
	1178	-C(O)-OCH ₂ - ⁵		Not observed
ν (C-O) in triglycerides ester linkage	1164 (1170 after ageing)	ν (C-O) in triglycerides ester linkage ^{2, 4, 34, 35, 36} + ν_{as} (C-O) of C-CO-O of higher aliphatic esters ³⁴	increase during oxidative polymerization ⁴	Increase
	1060-1150	ν (C-O-C) ethers ³		
	1140sh	shown, not discussed ⁴		
ν (C-O) in triglycerides ester linkage	1099	ν (C-O) in triglycerides ester linkage ^{2, 4, 34, 35, 36} + ν_{as} (O-CH ₂ -C) ^{2, 34}	increase during oxidative polymerization ⁴	Increase
	992	in tung oil: ω (CH) in CH=CH conjugated <i>cis</i> , <i>trans</i> , <i>trans</i> ³⁴		
<i>trans-trans</i> conjugated ω (C-H)	985 / 987	<i>trans-trans</i> conjugated ω (C-H) ^{3, 4, 5, 30, 31, 32}	form then decrease ^{5, 32} forms during thermooxidation, disappears during photolysis ³	Formation then decrease
	975	residual insaturation, monounsaturated fatty acids chains ^{14, 34}	disappear fast in the first h. of irradiation.	
non conjugated <i>trans</i> (C-H)	968 / 970	<i>trans</i> CH in C=CH /out of plane deformation ^{35, 41} /non conjugated ^{5, 30, 32} /non conjugated ω ^{3, 34} / non conjugated out of plane deformation ⁴	Form, increase ^{5, 32} increase over heating ³⁵	increase (then decrease slightly)
	965	in tung oil: ω (CH) in CH=CH conjugated <i>cis</i> , <i>trans</i> , <i>trans</i> ³⁴		
<i>trans-cis</i> conjugated ω (C-H)	947 / 950	ω (C-H) ^{3, 4, 5, 31, 32, 37} in <i>trans-cis</i> conjugated C-H=C-H	<i>cis</i> decrease by oxidation / conversion to <i>trans</i> (970) and conjugated (988 and 947) ⁴	decrease
Epoxide	885	Epoxide ^{3, 31} (<i>trans</i> epoxide) ⁴²		Formation then increase slowly
<i>cis</i> -C=(C-H)	722 / 723	<i>cis</i> (C-H) out of plane deformation ^{4, 33, 35} Rocking (CH ₂) _n - + ω (C-H)=CH ²	decrease. oxidation / conversion to <i>trans</i> (970) and conjugated (988 and 947) ⁴ decrease	decrease

		<i>cis</i> δ (-C=C-H) + CH ₂ skeletal vibration ^{5, 32}	decrease	
	720	Rocking (CH ₂) ^{34, 36}	decrease	
	716	γ -(C-H) ³	decrease	Not observed
	663	unsaturated cycles ³	appear at 60°C of thermolyzed and photolyzed samples	Not observed

The evolution of the FTIR spectra of the heated linseed oil without drier (H) is presented in Figs. 1 and 2. The quantitative evolution of the integrated area of characteristic peaks is reported in Fig. 3 (over 500 h) and Fig. 4 (zoom over 30h). The evolution of the peaks can be broadly separated in three steps: induction period (first few hours), transitory regime (increasing or decreasing exponential evolution, 6-100 h) and plateau or slight evolution.

In Fig. 2, three spectral zones have been selected to illustrate the main features, as presented by Mallegol *et al* [14]. From 3700 cm⁻¹ to 2750 cm⁻¹, oxidation and isomerisation processes are clearly visible. The broad band at ~3430 cm⁻¹ is assigned to hydroperoxides formed at an early stage of drying, and then to alcohols and ethers formed subsequently. The manifestation of this band allows us to estimate the induction time as it is accounted during the first steps of the *oxidation process* [2], i.e. around 8h as seen in Fig. 4. The decrease of the *cis* ν (C-H) in C=C-H bands (3010 cm⁻¹) is a marker of the *isomerisation process* consistent with the formation of radicals and the sequence of addition and elimination of hydrogen. The ν_a (C-H) bands in CH₃ (profile 2960) and in CH₂ (profile 2927) also decrease during drying. This decrease can be attributed to the loss of hydrocarbon after cleavage reactions [4] that yield volatile products in the early stages of the drying [43]. At longer times reticulation would also contribute as assumed by Ioakimoglou *et al.* [37] who even use this band to measure the extent of cross linking in oil with Cu-based driers.

The 1900-1500 cm⁻¹ region is centred on the carbonyl band, showing a strong broadening. The strong ν (C=O) ester peak shifts from 1744 cm⁻¹ to 1740 cm⁻¹ and broadens first at lower wavelengths, then at higher with the formation of secondary oxidation products

(more details in Table 3). The evolution of the ROI centred at 1710 cm^{-1} , attributed to different carbonyl groups such as aldehydes, ketones and carboxylic acids, illustrates this broadening that goes on even at longer times (Fig. 3). The small band at 1652 cm^{-1} decreases until complete disappearance (Fig. 2). It is assigned to $-\text{CH}=\text{CH}-$ vibrations but it is unclear whether it is only *cis* $-\text{CH}=\text{CH}-$ that contribute [4, 35] in which case this decrease is linked to the *isomerisation* process. At 1632 cm^{-1} , a small band is formed, attributed to conjugated $\text{C}=\text{C}$ [2, 4, 31] (Fig. 2). However, this band does not disappear at long-term which would make this assignment incomplete.

Also to be noted in Fig. 1, the global increase of the C-O stretching pattern (peaks at 1238 , 1164 and 1101 cm^{-1}) characteristic of the triglycerides ester linkages underlying their contribution during the drying process [4].

Finally the $1030\text{-}630\text{ cm}^{-1}$ region provides information about unsaturation bands and illustrates the *isomerisation* process. The broad *trans* $\text{C}=\text{C-H}$ band at 968 cm^{-1} increases through the first steps of drying. Then, after longer period of time it starts decreasing as seen in Fig. 2. On either side of this band, bands/shoulders are formed along drying at 950 and 985 cm^{-1} , related to conjugated double bonds (respectively *trans-cis* and *trans-trans*). They first increase and then decrease until they are completely hidden in the broad *trans* band. At 722 cm^{-1} non conjugated *cis* $\text{C}=\text{C-H}$ band decreases along drying (Figs. 2 and 3).

It is interesting to note that while the main evolutions in the FTIR spectra described in Table 3 occur before 5 days (the $\nu(\text{C-H})$ in *cis* $\text{C}=\text{C-H}$ *cis* peak has already completely disappeared for example), changes are still taking place over months (as the broadening of the $\nu(\text{C=O})$ peak, or the increasing of the whole $1400\text{-}600\text{ cm}^{-1}$ region).

Fig. 1: Evolution of the FTIR spectra of heated linseed oil (H) during drying as a 30µm film

Fig. 2: zooms on FTIR spectra of heated linseed oil (H) during drying as a 30µm film

Fig. 3: Evolution of FTIR peaks during the drying of 30 μm films of H (square, dark line) and HL_5 (circles, grey line). The name of the ROI is indicated above each graph: 3400 cm^{-1} (3136 - 3692 cm^{-1}), 3010 cm^{-1} (2988 - 3033 cm^{-1}), 1710 cm^{-1} (1672 - 1734 cm^{-1}) and 722 cm^{-1} (667 - 747 cm^{-1}). X-axis: time (h), y-axis: integrated intensity of FTIR absorption after subtraction of the first spectrum.

Fig. 4: Evolution of FTIR peaks during the drying of H (square), and oils treated with PbO at different concentrations HL_1 (star), HL_5 (circle), and HL_20 (triangle). The name of the ROI is indicated above each graph: 3400 cm⁻¹ (3136 - 3692 cm⁻¹), 3010 cm⁻¹ (2988 – 3033 cm⁻¹), 1710 cm⁻¹ (1672 – 1734 cm⁻¹) and 722 cm⁻¹ (667 – 747 cm⁻¹). X-axis: time (h), y-axis: integrated intensity of FTIR absorption after subtraction of the first spectrum.

3.2. Influence of oil treatment: FTIR characterisation before drying

Some chemical and physical modifications induced by treating oil with PbO have already been reported in the literature, focusing on different aspects: the chemical composition [44, 45], the kinetics of saponification [18, 20], and the rheological properties of the oils obtained [26]. In order to compare the evolution of the systems through drying, the FTIR spectra have been acquired after preparation but before any drying took place and they are presented in Fig. 5. This figure allows assessing the effect of PbO (HL vs. H), of its concentration (HL_1, HL_5 and HL_20), of the addition of water (HL_5 vs. HLw_5) and of heating (HL_5 vs HL_amb_5). The integrated intensities of the main ROI are indicated in Supporting

Information (Table S1) for each initial condition, before drying. The $\nu(\text{OH})$ domain is scarcely affected by the different treatments. Conversely, the $\nu(\text{CO})$ region shows strong modifications (ROI 1101, 1164, 1238, 1530, 1710, and 1746). In all cases with PbO, and to a much greater extent after heating, the formation of lead soaps is visible in the FTIR spectra by additional absorptions at 1530 and 1397 cm^{-1} corresponding respectively to the asymmetric and the symmetric stretching of lead carboxylates [18, 39]. When increasing the PbO content (1, 5, 20), these bands increase while the ester $\text{C}=\text{O}$ peak at 1746 cm^{-1} and the “ester triplet” (1240, 1160 and 1099 cm^{-1}) decrease. When adding water to the process, the soap bands increase as expected but the effect on the other bands is quite limited (Fig. 5 and Table S1). At low Pb content (PbO: HL_1 or PbCO_3 : HC_1) and without heating (HL_amb_x, x=1, 5 and 20), the spectra are quite similar to the heated oil without Pb (H). The FTIR spectra have been done in the first hour after mixing.

Changes at low wavenumbers are highlighted in Fig. 6. The *trans-trans* conjugated peak at 985 cm^{-1} is not visible in the H spectrum whereas it is for oil mixed with PbO, and it increases with the PbO content (it is even higher than the isolated *trans* peak at 968 cm^{-1} for PbO 20 %).

Fig. 5: FTIR spectra of treated oils, after preparation and before drying.

Fig. 6: zoom on a selection of spectra from Fig. 5

3.3 Influence of oil treatments on the drying process

3.3.a FTIR spectra of the oil + PbO 5 % system (HL_5)

Films of medium prepared by heating linseed oil with 5 % PbO (HL_5) have been analysed upon drying and FTIR spectra are presented in Fig. 7 and 8.

Fig. 7: Evolution of the FTIR spectra of linseed oil heated with PbO 5% (HL_5) during drying as a 30 μ m film.

Fig. 8: zoom on spectra shown in Fig. 7

From a qualitative point of view, the comparison of Figs. 7 and 8 (HL_5) with Figs. 1 and 2 (H) shows that the two series of spectra exhibit the same characteristic features: increase of the $\nu(\text{OH})$ absorption and broadening of the prominent $\nu(\text{C}=\text{O})$ absorption bands as *oxidation* markers, and decrease of the *cis* $\text{C}=\text{C}$ absorption bands and increase of the *trans* $\text{C}=\text{C}$ peaks illustrating the *isomerisation*. Also in the region $1030 - 630 \text{ cm}^{-1}$, the modifications of unsaturation bands are similar with and without lead drier, conversely to what had been observed for Co-drier [5] for which the vibration bands of conjugated compounds were more easily observed. Here the evolution of the triplet 985 (*trans-trans*), 970 and 950 (*trans-cis*) cm^{-1} is similar with and without lead. However the epoxide band at 885 cm^{-1} , is far more visible (after 29 h) than without lead drier. We conclude from these qualitative observations that the mechanism of oil drying in presence of Pb-drier belongs to oxidative polymerisation [1-5].

If the spectral evolutions are rather similar with and without PbO , the kinetic is clearly different (Figs. 3 and 4). With 5% PbO , the $\nu(\text{OH})$ absorption band can be observed much earlier, after approximately 3 hours (profile 3400 in Figs. 3 and 4), as compared to linseed oil alone for which the band is visible only after c.a. 10 h. Also characteristic of the *oxidation*

process, the broadening of the carbonyl band is accelerated and starts after 3-4 h of drying for HL_5, vs. 8-10 h for H (1710 cm^{-1} Figs. 3 and 4). It can be noticed that for both bands the final value reached after 500 h is the same, with and without PbO (Fig. 3). Hydroperoxides decomposition is also accelerated in the presence of the PbO drier, leading to a faster formation of secondary oxidation products (widening of the $\nu(\text{C}=\text{O})$ peak at higher wavenumbers occurring faster).

Likewise, the *isomerisation* and conjugation processes occur at a faster rate. The decrease of the *cis* C=C absorption band, at 3010 cm^{-1} , 722 cm^{-1} (and 1652 cm^{-1}) starts after 3 h with the addition of PbO, while it starts after about 10 h without PbO (Fig. 4). The formation and increase of the 1632 cm^{-1} band, and the evolution of the bands/shoulders at 950 and 985 cm^{-1} , all related to conjugated double bonds, are also accelerated. The maximum of the *trans-trans* conjugated CH=CH band at 985 cm^{-1} is reached after c.a. 50 h for H whereas it is reached after 4-5 h for HL_5.

Finally the comparison of Fig. 2 and Fig. 8 indicate that the decrease of $\nu_{\text{as}}(\text{C-H})$ bands in CH_2 and CH_3 groups is more pronounced with PbO addition in the first steps of drying (shoulder at 2960 no more visible after 7h for HL_5, whereas it is still present after 48h for H), on the contrary to what have been observed with copper salts in Ioakimoglou *et al.* [37]. As the authors attributed this decrease to a loss due to reticulation, they deduced that Cu-driers promote oxidative reactions but limit cross-linking. Here, we can state that the formation of volatile products and/or the reticulation (depending on the interpretation of the decrease of these bands, see table 3) is promoted by the use of PbO drier.

In conclusion, with the introduction of PbO, the induction period is reduced from 8-10 h for H to 2-3 h for HL_5. The transitory regime is more difficult to define precisely but is globally reduced from almost 100 h for H to 10-30 h for HL_5 (Fig. 3). With regards to the FTIR spectra, it appears that treatment with PbO only provokes an increase in drying rate, with

reduction of the induction time and increased speed of reactions, but does not modify drastically the mechanism of reactions and the final composition (similar evolution of the peaks and close values of the peaks in the “plateau” regime). It appears to be the same as observed for Co drier [14].

3.3.b Influence of PbO concentration upon drying

The FTIR spectra evolution has also been investigated for PbO 1 and 20 % (HL_1 and HL_20) in order to investigate the influence of Pb drier concentration (initial spectra in Fig. 5 and evolution in Fig. 9). The integrated intensity of some peaks is indicated in Fig. 4 (over 30 hours): the increase of $\nu(\text{OH})$ band (profile 3400 cm^{-1}), decrease of $\nu(\text{C-H})$ and angle deformation in *cis* $\text{C}=\text{C-H}_{\text{cis}}$ (profile 3010 and 722 cm^{-1} respectively) and broadening of the $\nu(\text{C}=\text{O})$ band (profile 1710 cm^{-1}) have been chosen as they give information about the first steps of drying. The evolution of the peaks attributed to lead soaps is quite difficult to determine quantitatively in HL_20 due to the complexity of the many spectral features in this area. The ROI profile method is not convenient for these bands and it was not possible to identify on the raw spectra whether there is an evolution specifically linked to the soaps.

For all the investigated concentrations, the same mechanisms are followed through drying as for the H condition. The evolution of the spectra is the same for PbO 1 % and 5 % with a slightly faster reaction for PbO 5%, and a shorter induction time for both *oxidation* and *isomerisation* processes; respectively indicated by the 3400 cm^{-1} ($\nu(\text{O-H})$ increase) and 3100 cm^{-1} ($\nu(\text{C-H})$ in *cis* $\text{C}=\text{C-H}$ decrease) profiles. At PbO 20 %, the global evolution is rather similar but small differences can be noted.

- The peak formed at long drying time at 1632 cm^{-1} for HL_1 and HL_5 shifts to lower wavenumber (1622 cm^{-1}) for HL_20 probably due to different coordination structures lead carboxylates. Meilunas *et al.* [4] observed such a peak in aged oil when lead white is present, and attributed it to the formation of lead carboxylates. Weerd *et al.* [36] observed bands

between 1630 and 1626 cm^{-1} in aged paints of oil with lead white pigments and at 1620 cm^{-1} with zinc white pigment.

- Moreover the epoxide band at 885 cm^{-1} is much more visible as well as the deformation of the conjugated C=C bands (*cis-trans* at 950 cm^{-1} and especially *trans-trans* at 985 cm^{-1}) already visible just after the film application and quite intense during the first hours.

- Peaks at 775 and 665 cm^{-1} are also visible; the last one having already been noticed by Mallegol *et al.* [3] for thermolysed and photolysed samples (assignment: unsaturated cycles).

If one compares the drier efficiency in terms of decreased induction time compared to H films, 5 % PbO content induces the best efficiency (Fig. 4). There is an optimal lead soap concentration as mentioned in Tumosa and Mecklenburg review [13]: « Early workers found a range of 1.0 % to 2.0 % metal per weight of oil to be the most effective concentration for lead, although its effectiveness in decreasing drying time was reached at about 0.3 % ». At 20% PbO, the film appears very viscous along drying which obviously prevented painters to use it at such concentrations: the prepared oil was to be added to colours on the artist's palette.

Fig. 9: Evolution of selected area of the FTIR spectra of HL_20 (top) and HL_1 (bottom) during drying as a 30 μ m film.

3.3.c Influence of the heating process

To evaluate the effect of the heating process during the preparation of the lead media, the same oil - PbO mixtures (1, 5 and 20 % of PbO) were prepared at room temperature and the drying process followed similarly. This process is not mentioned in the historical recipes (as seen in Table 1): when used as a drier, the litharge is mixed to the oil (while heating or at room temperature) and then let to settle down. The remaining litharge, if there is, has to remain at the bottom of the container and the upper mixture of oil and lead soaps is then used. Here the litharge is present in the applied film: we wanted to investigate the effect of litharge if added as a pigment, i.e. at room temperature without heating process nor long time settling. Litharge is present in the film along drying, and acts as a drier as well as the lead soaps

progressively formed in the film (as explained in 3.2).

We observe at all concentrations a faster drying than without PbO through both *oxidation* and *isomerisation* processes (Fig. 10). The concentration of PbO does not modify greatly the drying process, even at short times; the peak areas show slight variations between the different concentrations. No optimal concentrations could be found but the results suggest a faster oxidation with PbO 5 and 20% than with 1%. More surprisingly, the induction time is close with and without heating (Figs. 4 and 10), and at 1% PbO the reaction would be even faster without heating. The siccative action is not improved by adding PbO while heating. However painter would rather use oils prepared with heating process (or settling down) for colour and texture considerations. When PbO is added at room temperature without heating, it strongly modifies the oil colour (into an orange liquid) and translucency; **whereas when the oil is heated with PbO, PbO dissolves to form lead soaps soluble in oil**. The medium turns rapidly from an orange to a whitish mixture and the oil obtained is homogeneous (at least at low Pb content, and just after preparation) and translucent when applied as a film [46].

Fig. 10: Evolution of FTIR peaks during the drying of H (square), and oils mixed with PbO at ambient temperature at different concentrations HL_amb_1 (star), HL_amb_5 (circle), and HL_amb_20 (triangle). The name of the ROI is indicated above each graph: 3400 cm^{-1} ($3136 - 3692\text{ cm}^{-1}$), 3010 cm^{-1} ($2988 - 3033\text{ cm}^{-1}$).

3.3.d Influence of the lead-based compound

We also studied films containing 1% of PbCO_3 (HC_1), cited in numerous historical recipes as a siccative. A decrease of the induction time (both *oxidation* and *isomerisation*) compared to oil is also observed (Fig. 11). However the spectral evolution during drying is much slower than with PbO . It confirms the siccative action of *ceruse*, introduced as a pigment or a siccative by the artist and explains the predominant use of litharge as lead siccative.

Fig. 11: Evolution of FTIR peaks during the drying of FH (square), oil treated with PbO 1% DH_1 (star), and with PbCO_3 1% P_1 (circle). The name of the ROI is indicated above each graph: 3400 cm^{-1} ($3136 - 3692\text{ cm}^{-1}$), 3010 cm^{-1} ($2988 - 3033\text{ cm}^{-1}$).

3.3.e Influence of the addition of water

Water can also be used during oil treatment, either in washing steps, either during the oil treatment with litharge as mentioned in several recipes cited Table 1. According to Bonaduce *et al.* [45] who investigated the effect of several oil treatments on the oil composition, washing with water removes the antioxidants producing a more crosslinked and oxidised oil.

Here we evaluate the influence of the water addition while heating on the drying process: the water in excess is removed after the heating process but most of it has evaporated. Films were prepared with and without water at 5 % of PbO (HL_5 and HLw_5). However no difference in terms of changes in the FTIR spectra could be observed. The induction time is consistent with 3-4 h and the changes described previously without water are relevant to this sample as well. The increase of the saponification process induced by the addition of water was not sufficient to induce a visible change in the FTIR spectra evolution; no was the possible

removal of antioxidants by this addition of water sufficient. The importance of the addition of water while heating in historical recipes can be explained by the rheological and optical properties of the oil obtained [26]: even at high lead content (20 % of PbO), the prepared oil remains yellow and still flows (without water addition, the oil turns brown-black and does not flow at rest).

Fig. 12: Evolution of FTIR peaks during the drying of H, oil treated with PbO 5% HL_5 with and without water. The name of the ROI is indicated above each graph: 3400 cm⁻¹ (3136 - 3692 cm⁻¹), 3010 cm⁻¹ (2988 – 3033 cm⁻¹).

4. Conclusion

FTIR has been used to investigate the effects of lead oxide on the drying process of linseed oil and has proven its true action as a siccative. As a comparison, we firstly investigated heated oil without PbO. An extensive review of the literature in the field has been made to ensure the assignment of most peaks of the spectra (few remain unclear due to disagreement in publications). The addition of lead compounds and especially lead oxide accelerates the drying process and reduces the induction time, but without major change in the mechanisms involved and in the final composition. According to the FTIR spectra, no reaction path is favoured on the contrary to what could be observed with Cu compounds: oxidation, isomerisation, conjugation and even cross linking processes are all accelerated. An optimal concentration of 5 % PbO was found compared to 1 and 20 %. In depth investigations,

including different film thicknesses, would complete this study to state whether the siccative is acting on the whole paint film and differentiate it from surface driers.

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