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A multi-analytical approach to studying binding media in oil paintings

Characterisation of differently pre-treated linseed oil by DE-MS, TG and GC/MS

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Abstract This article presents a multi-analytical approach to investigating the drying, polymerisation and oxidative degradation of linseed oil, which had undergone various treatments known to be undertaken during the nineteenth century in preparation for painting. The oil was mechanically extracted from the same seed lot then processed by different methods: water washing, heat treatments, and the addition of driers, with and without heat. The oil was prepared in 1999 within the framework of the MOLART project. We compared thermogravimetric analysis (TG), which yields macromolecular information, with gas-chromatography mass-spectrometry (GC/MS) and direct exposure mass spectrometry (DE-MS), which provide molecular information. This comparison enabled us to elucidate the role of pre-treatment on the composition of the oil. TG and oxygen uptake curves registered at a constant temperature helped us to identify the different physical behaviour of the oil samples, thus highlighting the presence of hydrolysed, oxidised and crosslinked fractions, as a consequence of the different pre-treatments. GC/MS was used to characterise the soluble and non-polymeric fraction of the oil, to calculate the ratios of palmitic to stearic acid (P/S), and azelaic to palmitic acid (A/P), and to further evaluate the effects of oil pre-treatments. DE-MS using chemical ionisation with CH_4, enabled us to establish the chemical composition of the oil in different stages of ageing. DE-MS proved to be a useful tool for a simultaneous semi-quantitative characterisation of the free fatty acids, monoglycerids, diglycerides and triglycerides present in each sample. The combination of thermal analysis with GC/MS and DE-MS enabled a model to be developed, which unravelled how oil pre-treatments produce binders with different physical–chemical qualities.

Keywords Linseed oil · TG · DE-MS · GC/MS · Oil pre-treatments

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Introduction

The appearance of paint, its texture and flow properties, and the role of the artist in achieving that appearance cannot be addressed exclusively through a scientific analysis of paint samples from historic works of art. The particulars of paint formulation, including additives from

colourmen as well as the artist, and the painting's subsequent environmental exposure all contribute to a series of variables that complicate the analysis of the data obtained. Therefore, to begin to understand the role of individual factors, such as oil pre-processing and oil/pigment interactions in the ageing and mechanical behaviour of paint requires modelling. The oil used in this study was sourced from a single seed lot, extracted with a stainless steel custom built oil press and pre-treated using representative oil processing recipes (resulting from a comprehensive search of historic documentary sources) [1]. A benefit of following this route is that paints created with the differently treated oils provide insight into the artists' first-hand experience with their materials, what governed both their choices and the final appearance of the work [2].

Drying oils are mixtures of triglycerides, and contain smaller amounts of other compounds such as sterols and vitamins. Oils are classified as drying oils when they dry chemically to form solid films on exposure to air. Of the drying oils used as binders, linseed oil is the most common, with an excellent performance in terms of the dispersion of pigments, drying time, optical transparency, and stability of the film produced [3].

Drying oils are characterised by a high content of unsaturated fatty acids (>50%) [3]. With exposure to light and oxygen, these unsaturated fatty acids undergo oxidation and crosslinking reactions, leading to the formation of a strong elastic film, which is insoluble in water and in many organic solvents. Mono-unsaturated and poly-unsaturated compounds undergo several reactions with ageing. These are mainly radical reactions, which are light initiated, and are metal catalysed. As a result, a crosslinked fraction and oxidation products (partially lost by evaporation) are formed. The uptake of oxygen by double bonds leads to the formation of new oxygen-containing functional groups such as keto groups, and then to the oxidative cleavage of fatty acid hydrocarbon chains. As a result α,ω-dicarboxylic fatty acids (pimelic, suberic, azelaic and sebacic acids) are formed, azelaic being the most abundant [4–6].

On the other hand, radicals generated during the ageing of the dried paint film due to exposure to light can react with each other leading to the formation of crosslinked species [7]. Another effect of ageing is a decrease in extractable triglycerides [5, 6, 8, 9].

Painters were advised to pre-treat their oil to clarify it and enhance its drying characteristics, and to reduce its initial colour. Some common pre-treatments include water washing (for the removal of water-soluble components or mucilage), and heating with or without the addition of driers (metallic compounds) [1, 10].

Pigments, oil processing, and the use of extenders and artists' mediums all affect the way a given paint behaves during application, as well as the chemical composition of the oil film obtained and its future appearance. High molecular mass crosslinked triacylglycerols are formed; double bonds isomerise; highly unsaturated molecules disappear; oxygen is added; and dimers are formed due to Diels–Alder cyclisation [11, 12]. As a result of double bond isomerisation, suberic and sebacid acids increase with respect to azelaic acid, and they may indicate whether or not the oil has been pre-polymerised by heat treatment [5, 13–15].

This article focuses on an analytical study aimed at understanding what molecular changes are undergone by a linseed oil that has been subjected to different processing methods. Samples of the oil pre-treated in a number of different ways were analysed by thermogravimetric analysis, TG, direct exposure mass spectrometry, DE-MS, and gas chromatography mass spectrometry, GC/MS.

Thermogravimetric analysis (TG) collects changes in mass as a function of time or temperature. Weight loss is due to different reactions such as dehydration, decomposition, degradation, pyrolysis, combustion or oxygen uptake and is related to the purge gas flow employed (N_2, air, oxygen, etc.). Thermal analysis techniques can be used to investigate the thermal stability of oils in general and linseed oil in particular. Oxidative mechanisms occurring in the degradation of linseed oil have been studied by TG and DSC, supported by other techniques, such as FTIR and SEC in a multi-analytical approach [16]. DSC and TG enabled the thermal stability of samples of linseed oils treated at a constant temperature for a prolonged time to be investigated. On the basis of a comparison between the DSC and TG curves, it was possible to identify the various steps in the thermo-oxidative degradation of linseed oils. This article contributes significantly to knowledge of the chemical processes involved, and provides data which can contribute the understanding of previous [17] and ongoing [18] studies of the present-day appearance of nineteenth-century paints.

DSC and TG have successfully been used in the field of cultural heritage [19, 20]. There are studies based on DSC analysis that investigate the role of the pigments and driers on the oxidative reactions taking place in the polymerisation of linseed oil. They show that, polymerisation reactions are accelerated by a temperature increase and the presence of inorganic pigments. such as minium (Pb_3O_4), chrome yellow ($PbCrO_4$) and lead–tin yellow ($PbSnO_4$) [21] and metal driers, such as zirconium and manganese driers [22]. The role of antioxidants on the oxidative stability of linseed oil has been investigated through a thermoanalytical study based on DSC and TG [23]. From the DSC curve, the onset temperature was identified at which the autoxidation process begins. This temperature is a parameter to evaluate the oxidative susceptibility of oils [24–26].

DE-MS is based on desorption/pyrolysis mass spectrometry and it can identify the nature of the main molecular constituents and provide a fingerprint together

with general information on the nature of the organic materials [27, 28]. In this article, DE-MS was employed to detect the occurrence of tri-, di- and monoacylglycerols, as well as the presence of free fatty acids [28], thus providing an indication of the degree of hydrolysis of the medium.

Finally, GC/MS was used to quantitatively and qualitatively evaluate the differences between the oil media after saponification, in terms of saturated and unsaturated fatty acids, dicarboxylic acids and other intermediate oxidised fatty acids, thus enabling a good comparison of their oxidation levels [29].

In this article, a systematic study is presented on linseed oil that had been extracted from a single seed lot using a stainless steel oil press. Various historical recipes for preprocessing the oil before its use in paint were then followed (MOLART project [1]). These included processing with and without heat, with and without lead-based driers (lead (II) oxide, lead acetate trihydrate, and lead subacetate), and with or without water washing. This oil with its eight different pre-treatments had then been used in hand-grinding a series of paints with lead white, vine black and umber pigments. The lead white paints exhibited distinctly different rheologies and colour [30], while, when vine black was used, not many variations were observed between paint replicas made with oils processed using different methods [1]. This study reports on findings related to state of the oil, and discusses the degradation of antioxidants taking place when the oil is washed, the oxidising and crosslinking effects of heating and treatment with lead-based driers, as well as the hydrolysing effects caused by the addition of the lead-containing species.

Materials and methods

Reagents

All the solvents were Baker HPLC grade and were used without any further purification. *N,O-bis*(trimethylsilyl)trifluoroacetamide (BSTFA) was purchased from Sigma-Aldrich (USA).

The following solutions were prepared by weighing pure substances and were used as standards: tridecanoic acid solution in isooctane (Sigma-Aldrich (USA), purity 99%), 135.48 μg/g, was used as a derivatisation internal standard; hexadecane solution in isooctane (Sigma-Aldrich (USA), purity 99%), 80.34 μg/g, was used as an injection internal standard; mono and dicarboxylic acids solution in acetone, containing lauric acid (0.24 mg/g Lau), suberic acid (0.27 mg/g, Sub), azelaic acid (0.28 mg/g, A), myristic acid (0.25 mg/g, Myr), sebacic acid (0.3 mg/g, Seb), palmitic acid (0.25 mg/g, P), oleic acid (0.51 mg/g, O), and stearic acid (0.51 mg/g, S) were used for the quantitation of the different compounds in the chromatograms. All acids, purity 99%, were purchased from Sigma-Aldrich (USA).

Standards

Stearic acid, DL-α-Palmitin, 1,2-Dipalmitolyl-glycerol, Tripalmitin, were supplied by Sigma-Aldrich (USA), all with a purity >99%.

Apparatus

A microwave oven model MLS-1200 MEGA Milestone (FKV, Sorisole, Bergamo, Italy) was used for the saponification of glycerolipids. Operating conditions were as follows: 80 °C, 200 W, 60 min.

A 6890N GC System Gas Chromatograph (Agilent Technologies) was coupled with a 5973 Mass Selective Detector (Agilent Technologies) single golden quadrupole mass spectrometer, equipped with PTV injector. The mass spectrometer was operated in the EI positive mode (70 eV). The MS transfer line temperature was 280 °C; the MS ion source temperature was kept at 230 °C and the MS quadrupole temperature at 150 °C. For the gas chromatographic separation, an HP-5MS fused silica capillary column (5%diphenyl-95%dimethyl-polysiloxane, 30 m × 0.25 mm i.d., 0.25-μm-film thickness, J&W Scientific, Agilent Technologies, Palo Alto, CA, USA) coupled with a deactivated silica pre-column (2 m × 0.32 mm i.d., J&W Scientific Agilent Technologies, Palo Alto, CA, USA) using a quartz press fit was used. The carrier gas was used in the constant-flow-rate mode (He, purity 99.995%) at 1.2 mL/min. The PTV injector was used in splitless mode at 300 °C, and the chromatographic oven was programmed as follows: 80 °C isothermal for 2 min, 10 °C/min up to 200 °C, 200 °C isothermal for 3 min, 10 °C/min up to 280 °C, 280 °CC isothermal for 3 min, 20 °C/min up to 300 °C isothermal for 30 min.

Chromatograms were acquired in both total ion chromatogram (TIC) and selected ion-monitoring (SIM) modes. Quantitative analyses were performed in SIM mode using calibration curves and daily injections of standards to evaluate changes in the response of the instrument.

DE-(CI)MS: The sample (a few nanograms) was placed on the rhenium filament at the end of a probe. The heating of the probe was operated in current-programmed mode, with a maximum current of 1000 mA, which corresponds to approximately 1000 °C. The conditions to obtain a Total Ion Current (TIC) curve as a function of time were obtained by programming the probe as follows: 0 mA for 20 s, from 0 to 1000 mA in 2 s, then 1000 mA for 60 s. A mass spectral fingerprint was obtained by averaging the mass spectra in the desired time range. The desorbed material was ionised by chemical ionisation (methane,

Table 1 Description of the oils analysed and their processing methods

Name	Description	Processing	Observations
Z	Freshly pressed Linseed oil in 1999—untreated oil	Cleaned flaxseeds were ground—the ground meal was pressed	Oil yield was approximately 22–23%.
X	Fresh oil (Z) washed in purified water	Freshly pressed oil and purified water were periodically shaken with the water regularly changed over a period of 3 weeks—oil was filtered	
ZH150	Fresh oil (Z) heated up to 150 °C	Freshly pressed oil was heated up to 150 °C—temperature was reached in approx. 15 min, and the oil was then allowed to cool	During heating no movement or colour change was observed in the oil.
ZH300	Fresh oil (Z) heated up to 300 °C	Freshly pressed oil was heated up to 300 °C—temperature was reached in about 60 min, and the oil was then allowed to cool—the cold oil was filtered	Active boiling was reached at 277 °C—charred particles, a white smoke and yellow deposits were produced—the oil had a strongly acrid smell—the oil had a dark colour
B8	Fresh oil (Z) + Lead acetate	Freshly pressed oil was periodically shaken together with lead acetate trihydrate over a period of 3 days—the oil was then decanted	
C8	Fresh oil (Z) + Lead subacetate	Freshly pressed oil was periodically shaken together with lead subacetate over a period of 3 days—the oil was then decanted	
CH8	Fresh oil (Z) + Lead subacetate heated up to 150 °C	Freshly pressed oil was mixed with lead subacetate and heated up to 150 °C, and then left to cool—the cold oil was then decanted	Active boiling was reached at about 140 °C—orange spots formed—oil became cloudy—a white deposit formed
AH2	Fresh oil (Z) + Lead(II) oxide heated up to 150 °C	Freshly pressed oil was mixed with litharge (lead (II) oxide) and heated up to 150 °C, and then left to cool—the cold oil was then decanted	Oil slowly became cloudy—a white deposit formed

1.0 mL s^{-1}) in a Thermo Finnigan Polaris Q ion trap mass spectrometer (ion source temperature of 250 °C), and a total ion current was acquired as a function of time. The mass spectrometer was scanned over an *m*/*z* range of 50–1000.

A Perkin Elmer Thermobalance model TG7 was employed. Two kinds of experiment were carried out: (a) isothermal experiments at 80 °C under a constant flow (90 mL/min) of air; b) dynamic experiments at a constant rate of 20 °C/min, from 50 to 700 °C. Measurements were performed under a constant flow (90 mL/min) of air or nitrogen. All the curves were normalised by subtracting the background (the empty crucible). The amount of sample in each measurement varied between 1.7 and 2.4 mg.

Samples

As noted above, the linseed oil had been prepared within the framework of the MOLART project [1, 2]. The oil was extracted mechanically using a stainless steel custom built oil press. Linseeds were from the same seed lot organically grown in the Netherlands [2]. Each differently processed sample of the oil was then stored in closed glass bottles (closely filled to reduce contact with oxygen and stored primarily in the dark). A description of the oil processing is summarised in Table 1. For more detailed information see the MOLART report [1].

Results and discussion

Characterisation of the untreated oil (Z)

Although it is known that, under ageing, a drying oil is subject to hydrolysis, crosslinking and oxidation reactions, DE-MS analysis of this sample revealed that triglycerides were still abundant and preserved. Figure 1 shows the mass spectrum of sample Z.

The complexity of the mass spectrum reflects the complexity of the chemical composition of the oil, over 95% of which is known to be made up of triglycerides with acyl moieties with several double bonds (up to 9 in the case of triacylglycerol of linolenic acid). The mass spectrum shows three clusters of molecular ions, corresponding to triacylglycerols, at *m*/*z* 802–812, 848–864 and 870–886.

The fragment ions, formed from triglycerides due to the loss of an acylium group ($[M\text{-}RCOO]^+$) and of an acylium group plus an additional hydrogen ($[M\text{-}RCOOH]^+$) are very intense and form two clusters at *m*/*z* 570–578 and 594–604, respectively. Important peaks are at *m*/*z* 341, 339,

Table 2 Characteristic parameters determined for the analysed oils

	P/S	A/P	Σ*D*
Z	1.4	0.0	0.1
X	1.4	0.0	0.2
B8	1.2	0.0	0.1
C8	1.8	0.0	0.3
ZH150	1.3	0.0	0.3
ZH300	1.2	0.0	0.3
AH2	1.4	0.3	5.6
CH8	1.8	0.0	0.3

337, 335 and 313. These latter peaks, corresponding to the fragment ions ($[RCO+74]^+$) with the glycerol backbone minus one hydroxyl group, provide information on the fatty moieties present in the triacylglycerols. Peaks at *m*/*z* 339, 337 and 335 show that unsaturated C18 fatty acids (oleic, linoleic and linolenic acids) are still present in the composition of the oil. The fragment ions ascribable to free fatty acids are not abundant in the mass spectrum, indicating that the hydrolysis of the triglycerides is not advanced. Finally, the peaks at *m*/*z* 91 and 105 are due to alkylated benzenes produced from the pyrolysis of the crosslinked oil paint material, thus indicating that crosslinking has taken place.

GC/MS analysis revealed the presence of saturated and unsaturated fatty acids, with palmitic and stearic acid being the most abundant saturated ones, and oleic, linoleic and linolenic being the most abundant unsaturated ones. Traces of sebacic, suberic and azelaic acids were present indicating that oxidation is taking place.

The characteristic parameters which are commonly used to characterise a lipid material, A/P, P/S and Σ*D* (ratio azelaic acid/palmitic acid; ratio palmitic/stearic acid; sum of dicarboxylic acid), are reported in Table 2. The P/S ratio can be employed to identify the source of the oil, and the A/P ratio and Σ*D* can be used as a measure of the oxidation taking place in a lipid material. This is because azelaic acid and other diacids originate from oxidation of the unsaturated fatty acids present in the oil [3].

The P/S data obtained are all in agreement with the values reported in the literature for a linseed oil [29]. This enabled us to conclude that the treatments investigated do not produce changes in the relative amounts of palmitic and stearic acids in the liquid oils, so as to prevent their identification.

TG enabled us to investigate the molecular mass distribution of the oil constituents. A comparison between the curves of thermal mass loss (and its derivative) for a linseed oil (Z) and some of its constituents is shown in Fig. 2.

Thermal degradation under a nitrogen flow for linseed oil starts at a higher temperature than for all of the oil constituents (mono-, di- and tri-glycerides and free fatty acids). This confirms that the oil is not strongly hydrolysed, as the peaks of thermal degradation of free fatty acids, monoglycerides and diglycerides have little effect on the features of the derivative curve of the oil. The main mass loss for the oil occurs at a higher temperature than that of triglycerides and the other standards. This indicates that in the oil there are species with a higher molecular mass than triglycerides (i.e. oligomers and oxidised compounds), in agreement with the literature [1].

The thermogravimetric curve under air flow of the untreated Z oil is reported in Fig. 3.

Four different steps in the thermo-oxidative degradation of linseed oil can be seen in Fig. 3: one at 150 °C, one at 350 °C and two above 400 °C. As discussed in the literature [16], the step at 350 °C corresponds to the first stage of oxidative decomposition and those above 400 °C correspond to the main processes of decomposition which give rise to a complete volatilisation.

The small mass loss occurring at 150 °C could either be due to the evaporation of a small amount of water bound to mucilage or to the oxidation of antioxidants present in the untreated Z oil.

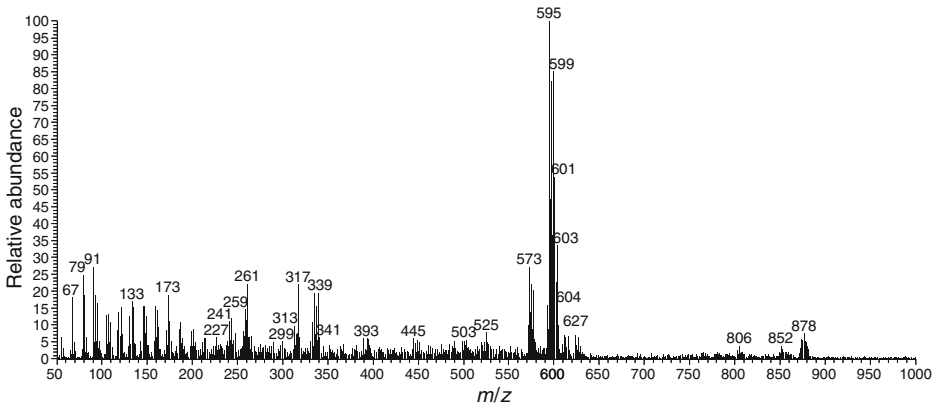

Fig. 1 DE-mass spectrum of sample Z (untreated oil)

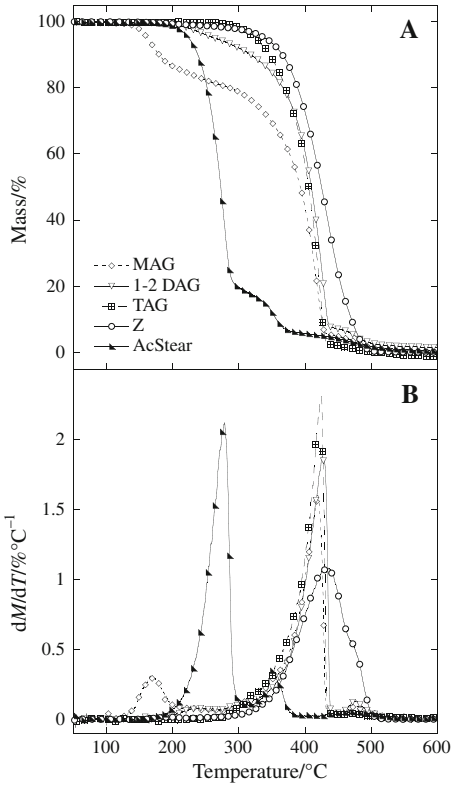

Fig. 2 Thermogravimetric curves (**a**) and their derivatives (**b**) under nitrogen at 20 °C/min heating rate of an oil (Z = untreated oil) and its constituents (MAG = DL-α-Palmitin; 1-2 DAG = 1,2-Dipalmitolyl-glycerol; TAG = Tripalmitin; AcStear = stearic acid)

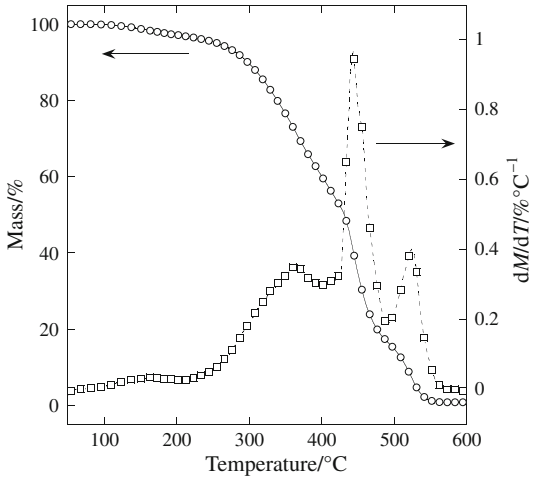

Fig. 3 Thermogravimetric curve (*left axis*) and its derivative (*right axis*) under air flow at 20 °C/min heating rate of Z oil (untreated oil)

The effect of washing with water

Washing the oil with water removes water soluble components, commonly referred to as mucilage, which contains mainly polysaccharides and proteins [31]. GC/MS results (Table 2) show that the water washed oil X is more oxidised than the untreated oil Z, as the Σ*D* of X is in fact slightly higher than Z.

This seems to indicate that the washing with water has removed compounds such as carotenoids and sterols, which are known antioxidants, even though they are hydrophobic. One possible explanation is that they are associated with the mucilage in the oil, and when this is removed, they are extracted as well.[1]

A comparison between the thermogravimetric curves and the corresponding derivative curves under nitrogen flow for the two oils is reported in Fig. 4a, b.

The thermal degradation of the untreated oil Z is shifted to higher temperatures than the washed one X, indicating the presence of species of a higher molecular mass. As it had been indicated by GC/MS, the washed oil X is more oxidised than the untreated oil Z. It is thus possible to conclude that the Z oil degrades at higher temperatures because some of its triglycerides are more crosslinked. The thermogravimetric analysis under air flow of the two oils is shown in Fig. 4c, d.

Washing with water strongly affects the thermogram of the oil. The X curve shows only three main steps, instead of four as in the Z curve: a step at 340 °C, one at 430 °C and one at 570 °C. The disappearance in the X signal of the small step at 150 °C could be due to the lack in the X oil of mucilage and antioxidants caused by the water washing. The shift of the step at 520 °C in the Z curve to higher temperatures (570 °C) in the X curve is probably due to the degradation of oxidised species (also highlighted by GC/MS), which require higher temperatures than the degradation of oligomers.

In conclusion, washing with water removes antioxidants together with polysaccharides and proteins. The absence of antioxidants produces an oil that is more oxidised than the untreated one. When mucilage is not removed, a lower oxidation is observed, but double bonds are partially consumed by crosslinking reactions. A certain amount of radicals are most likely generated during the extraction process, maybe simply as an effect of light exposure, as has been observed for triterpenoid resins [32]. Scavenging of these radicals is then influenced by the presence/absence of substances with antioxidant properties, which influence the degradation pathway of the oil triglycerides.

The role of lead based driers

The TG curves under nitrogen flow of the oils treated with lead acetate and lead subacetate are compared with that of the untreated oil in Fig. 5.

[1] Water washing takes place over six weeks, with the oil and water kept in a large glass container, it cannot be excluded that antioxidants are partially consumed in this period for contact with oxygen and light.

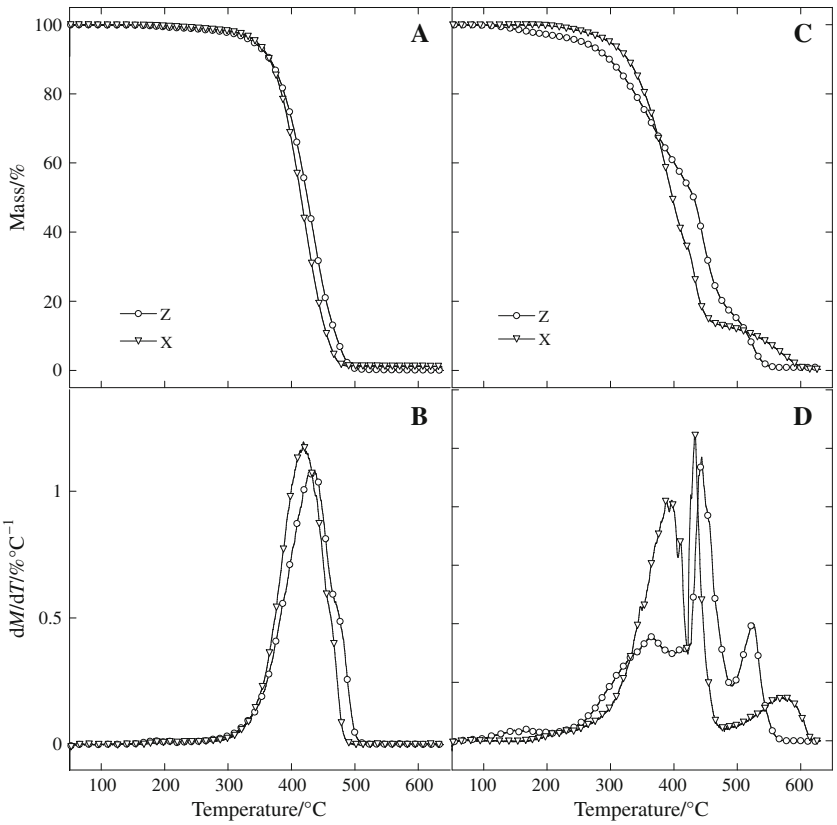

Fig. 4 Thermogravimetric curves (**a**: under nitrogen; **c**: under air) and their derivatives (**b**: under nitrogen; **d**: under air) at 20 °C/min heating rate of the untreated linseed oil (Z = untreated oil) and the water washed oil (X = water-washed Z oil)

The treatment of the oil with lead driers leads to results that are analogous to those obtained with water washing, i.e. the degradation occurs at lower temperatures. This could be explained by taking the procedure of preparation into account, which entails decanting the sample after mixing the oil with the drier. Antioxidants are most likely removed in this way. It should be noted that treatments with metal-based compounds [2] were used to remove mucilage from fresh pressed oils. It is also possible to hypothesise that lead in any form acts as a scavenger for free radicals, leaving less reactive molecules that are able to create the crosslinked network. The position of the maximum in the curve of the oil treated with lead acetate (B8) also suggests that hydrolysis is taking place. As far as oxidation is concerned, the use of lead subacetate (C8) seems to produce an oil with a slightly higher degree of oxidation, as can be inferred by the higher ΣD observed in sample C8 compared to the B8 and Z samples (Table 2).

The role of heat treatments

The TG curves and corresponding derivative curves under a nitrogen flow for three different oils (the Z oil, the Z oil heated at 150 °C, ZH150, and the Z oil heated at 300 °C, ZH300) are reported in Fig. 6a, b.

The behaviour of the three curves is quite similar, showing that the thermal treatment slightly affects the degradation temperatures. Only the mass loss curve of the oil heated to 300 °C (ZH300) is shifted slightly at a higher temperature than the untreated one (Z), thus indicating that it contains higher molecular mass components such as oligomers and oxidised compounds. The thermal treatment also influences the high temperature shoulder of the TG curves, as is reported in the inset of Fig. 6b. The process occurring at 470 °C is enhanced by the thermal treatments. The same mass loss step at 470 °C occurs in the thermograms of MAG and 1-2 DAG (see Fig. 3), which suggests a partial hydrolysis of the heated oils.

GC/MS results highlight that heat treatment favours oxidation, as both heated oils show a higher ΣD value compared to the untreated one (Table 2). This confirms a previous study that proved by using ESI-FTICR-MS and MALDI-MS, that oligomers and triacyglycerols with a higher number of incorporated oxygen TAGs were more abundant in heated oils than in untreated ones [11].

The synergistic role of the thermal treatment and lead (II) subacetate as observed by TG is shown in Fig. 6c, d. The thermal treatment of the oil with the drier added (sample CH8) produces quite a different oil than the unheated one (C8). The thermogram of the CH8 sample shows at least four main steps spanning from 200 to 600 °C, indicating the presence of a broad range of molecular mass compounds from low to relatively high. This means that heating in the presence of lead subacetate

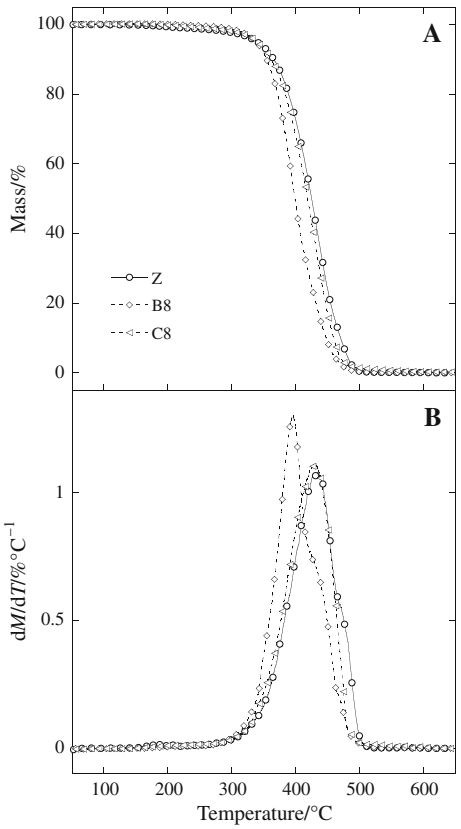

Fig. 5 Thermogravimetric curves (**a**) and their derivatives (**b**) of the untreated oil (Z = untreated oil) and the oils treated with lead-based driers (B8 = Z oil treated with lead acetate; C8 = Z oil treated with lead subacetate)

causes crosslinking and hydrolysis at the same time. This is also confirmed by the macroscopic behaviour of the CH8 sample during the preparation: in fact this oil showed a lower boiling point (140 °C) than the oil heated without the drier (ZH150) [1].

In terms of GC/MS, the use of lead subacetate seems to cause a more oxidised oil than the untreated oil, but no differences are observed between the CH8 and C8 oils (Table 2), as the degree of oxidation of the two oils appears to be the same ($\Sigma D = 0.3$).

It is also possible to observe the effect of heating in the presence of different lead-based driers.

As reported in Fig. 6e, f, the oil with litharge (AH2) added shows a step at high temperatures, which can be related to the presence of higher molecular mass compounds that are absent in the other two heated oils. Moreover, the position of the maximum in the curve of both the oil treated with litharge (AH2) and with subacetate (CH8) seems to suggest that hydrolysis is taking place. This cannot be seen by DE-MS analysis, and a comparison between the mass spectrum of AH2 and the mass spectrum of Z did not show a different degree of hydrolysis.

As the A/P and the ΣD values are higher for the AH2 oil than the CH8 oil (Table 2), it is possible to hypothesise that lead (II) oxide (litharge) favours oxidation.

The thermal treatment also causes the isomerisation of double bonds [11]. In the case of the oils under investigation, this effect is much more visible in the oil heated to 300 °C (ZH300). However, it is also observable in the chromatograms of the oils heated to 150 °C where there are several peaks due to isomerisation products of linolenic acid. This can be seen in Fig. 7 where the extracted ion chromatogram of *m/z* 335 (corresponding to the $[M\text{-}15]^{\bullet +}$ fragment ion of the trimethylsilyl ester of the acid with 18 carbons and 3 unsaturations) for the untreated and the heated oils are compared. In contrast, linoleic and oleic acids still seem stable under these conditions in the same oils, as no isomers are detected in the chromatograms. The chromatograms of the heated oils show several peaks (much more abundant in the ZH300), indicating that more than one isomer has been formed, corresponding to isomerisations taking place at more than one double bond. The high number of isomers observed clearly indicates that not only cis/trans isomerisation took place, but also double bond transpositions.

The higher number of isomers formed must be considered responsible for the dark colour of the oil heated to 300 °C (ZH300), as the isomerisation produces the conjugation of the double bonds that were originally non-conjugated in linoleic and linolenic acids. Extending conjugation, in fact, generally results in bathochromic and hyperchromic shifts in the UV-Vis light absorption of the oil.

Isothermal treatment at 80 °C

The oxygen uptake was monitored by following the mass changes in the thermobalance of the samples exposed at a constant temperature of 80 °C under air flow. This enabled us to investigate the effect of the oil treatment on the oxygen uptake, which is related to the oxidation and crosslinking state of the sample. Oxygen in fact is added to the double bonds of the unsaturated fatty acids. If the oil after treatment with a drier or heat, or a combination of both, is subjected to oxidation or crosslinking, the number of double bonds will be less than in the untreated oil.

The oxidation and crosslinking[2] of drying oils have been reported to be free-radical chain initiated, and propagation and termination are radical-based as well [7]. These radical reactions can consume double bonds, leaving an oil with a reduced capacity to uptake oxygen.

[2] Dimerisation and trimerisation can also occur as an effect of Diels–Alder cyclisation reactions [33].

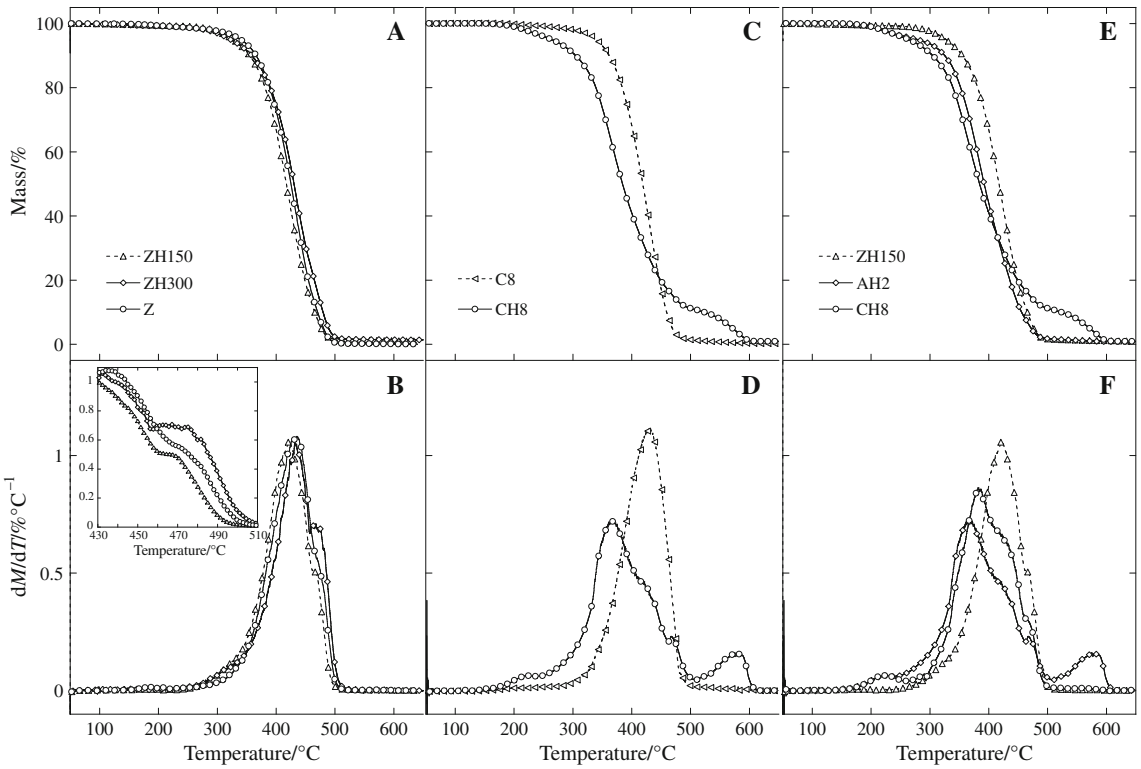

Fig. 6 Thermogravimetric curves (**a**, **c**, **e**) and their derivatives (**b**, **d**, **f**) in function of temperature of several linseed oils under nitrogen flow at 20 °C/min heating rate (**a** , **b**: Z = untreated oil; ZH150 = Z oil heated to 150 °C; ZH300 = Z oil heated to 300 °C); (**c**, **d**: CH8 = Z oil treated with lead subacetate and heated up to 150 °C; C8 = Z oil treated with lead subacetate); (**e**, **f**: ZH150 = Z oil heated to 150 °C; AH2 = Z oil with Lead (II) oxide then heated to 150 °C; CH8 = Z oil with Lead (II) subacetate then heated to 150 °C)

The oxygen uptake curves of some of the oils investigated are reported in Fig. 8.

In a previous study on fresh linseed oil, it was observed that the initial phase of oxygen uptake starts after an induction time due to the presence of antioxidants, which react with oxygen [16]. The untreated oil Z shows an induction time of approximately a few hundred minutes, indicating that antioxidants are still present, even though the oil was prepared more than 10 years before the analysis was performed. After the induction time, the oil starts increasing in mass, reaching a maximum of 10%, which can be explained as the addition of oxygen by the double bonds of unsaturated fatty acids [16]. Once the maximum is reached, the mass decreases. This phenomenon is likely due to secondary scission reactions forming small amounts of volatile compounds, as observed in the literature [16].

For the washed oil (X), the mass starts increasing almost immediately, without an induction time. This indicates that antioxidants are absent, confirming what was observed previously by TG. It is also possible to observe that for oil X, the amount of oxygen uptake is lower than oil Z, indicating that the number of double bonds present in the water-washed oil is lower than the untreated oil, due to the oxidation observed by GC/MS.

A comparison between the curves of the untreated oil and the heated oils without the lead-based driers reveals that heating causes some of the antioxidants originally present in the oil to be consumed, as the induction times of both ZH150 and ZH300 are lower than that of oil Z. The heating treatment also reduces the oxygen uptake of the two oils, the effect being more pronounced in the oil heated at 300 °C than the oil heated at 150 °C. GC/MS revealed that that the heated oils are more oxidised than the untreated oil, and TG highlighted that the oil heated to 300 °C is the most crosslinked. These factors take the reduced number of instaurations still present in the heated oils into account, and thus the oxygen uptake behaviour observed. This also explains the fact that the curves of the heated oils and the untreated oil intersect after prolonged storage under an air flow in the thermobalance at 80 °C. This is most likely because the fragments produced under prolonged storage at 80 °C by the fatty acids embedded within the polymeric network cannot escape the network itself, resulting in a reduced mass loss of ZH150 and ZH300 compared to Z.

Finally, the oil heated in the presence of litharge up to 150 °C (AH2) shows a similar behaviour as the oil heated to 300 °C, in terms of mass changes. The GC/MS and TG data

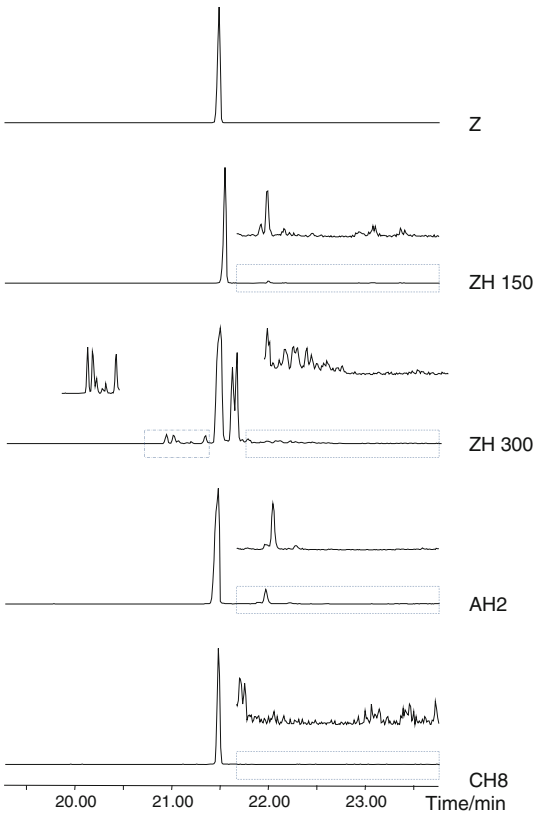

Fig. 7 Extracted ion chromatograms of the fragment ion *m/z* 335 of the untreated oil (Z) and the heated oils (ZH150, ZH30, AH2, CH8). The areas highlighted inside the dotted boxes are magnified immediately above each corresponding box

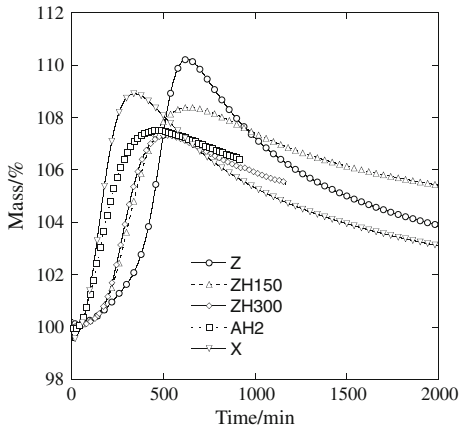

Fig. 8 Percent mass changes of several linseed oils (Z = untreated oil; ZH150 = Z oil heated to 150 °C; ZH300 = Z oil heated to 300 °C; AH2 = Z oil + Lead (II) oxide then heated to 150 °C; X = water-washed Z oil) treated under air flow at a constant temperature (80 °C) versus time of treatment

reported previously showed that the AH2 is more oxidised and less crosslinked than ZH300. This indicates that, although through different processes, the oil treated with litharge presents a similar consumption of double bonds as the oil heated at a higher temperature. The oil heated with litharge shows a much shorter induction time compared to the untreated oil and the other heated oils, and very similar to that of the washed oil. This suggests that litharge and heating caused a further depletion in antioxidants compared to heating alone. This confirms the historical documentary reports that driers were also added to the oils to remove mucilage and thus [10, 34], as observed in the case of water washing, to remove antioxidants as well.

Conclusions

Although the oil samples investigated are still liquid, they show a certain level of crosslinking, hydrolysis and oxidation. As the treated samples were obtained from the same oil, and they were stored in the same conditions, the different physico-chemical properties observed can be attributed to the different pre-treatments of the oils.

It is thus possible to draw some general conclusions:

- all the treated samples show a lower number of double bonds, producing oils that dry in less time than the untreated oil;
- oxidation is favoured by almost all treatments, with the exception of mixing the oil with lead acetate at room temperature. The strongest oxidising effect is caused by the combined use of litharge (lead (II) oxide) and heat.
- Hydrolysis takes places when the oil is either heated or treated with lead-based driers. The combination of the two treatments produces the most hydrolysed oils.
- Antioxidants are reduced by all treatments, with water washing and the combined use of litharge and heat being the most effective. The reduced amount of antioxidants makes drying quicker.
- Crosslinking is clearly observed after heating at 300 °C or at 150 °C in combination with lead-based driers. The lower number of double bonds present in a prepolymerised oil enables the medium to be dried more quickly.

As reported in the "Introduction" section, the oils analysed in this study were employed to prepare paint replicas, using lead white [$(PbCO_3)\cdot 2Pb(OH)_2$], umber [clay pigment which contains iron and manganese oxides] and vine black [C] as pigments [1]. Paints made with umber and vine black did not exhibit the same extreme range of rheological properties as lead white did according to the oil pre-treatments. The behaviour of the lead white paints is summarised as follows (the painters' term "short" refers to a buttery-textured paint, and "long" refers to a more fluid paint):

- Z short paint;
- X creamy (more viscous than Z, but not short);

- ZH150 short paint;
- ZH300 long paint (actually the paint was extremely runny);
- B8 short paint (very stiff);
- C8 short paint;
- CH8 long paint (quite runny);
- AH2 long paint.

Generally speaking, an oxidised and/or hydrolysed oil is a more polar binder, and would be expected to show different behaviours when combined with polar and non-polar pigments. As a result, the more homogeneous behaviour generally observed in the umber and vine black paints can be explained by considering that all the oil samples, despite the different pre-treatments, contain a major non-polar fraction that can homogeneously disperse umber or vine black. Lead white is an extremely polar pigment, in which the lead can give rise to strong complexes with carboxylates [2]. When mixed with the paint binder, if it contains polar groups, such as in an oxidised and/or hydrolysed oil components, it can be partly dispersed, but also partially solubilised, giving rise to a longer (more free-flowing) paint than that obtained when pigment dispersion is the primary phenomenon taking place. This explains why X, ZH300, CH8 and AH2 produce relatively a long paint compared to those obtained, respectively, with Z, ZH150, C8 and B8.

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