

Article

Oil Media on Paper: Investigating the Interaction of Cold-Pressed Linseed Oil with Paper Supports with FTIR Analysis

Penelope Banou ^{1,2,*} , Stamatis Boyatzis ¹ , Konstantinos Choulis ¹, Charis Theodorakopoulos ² and Athena Alexopoulou ¹

¹ Department of Conservation of Antiquities and Works of Art, University of West Attica, Egaleo, 12243 Athens, Greece

² Department of Arts, Northumbria University, Newcastle, Newcastle upon Tyne NE1 8ST, UK

* Correspondence: pbanou@uniwa.gr

Abstract: Previous works of the authors have presented the changes in the optical, mechanical, and chemical properties of the oiled areas of the supports that occur upon ageing due to oil-binder absorption in works of art on paper and printed material. In this framework, transmittance FTIR analysis has indicated that the presence of linseed oil induces the conditions to promote the deterioration of the oil-impregnated areas of the paper supports. However, the analysis of oil-impregnated mock-ups did not provide detailed information about the input of linseed oil formulations and the different types of paper support on the chemical changes that occur upon ageing. This work presents the results of ATR-FTIR and reflectance FTIR, which were used for compensating the previous results, proving indications on the effect of different materials (linseed oil formulations, and cellulosic and lignocellulosic papers) on the development of chemical changes, thus, on the condition of the oiled areas upon ageing. Although linseed oil formulations have a determining effect on the condition of the oiled areas of the support, the paper pulp content appears to have an input to the chemical changes that occur in the system of paper–linseed oil upon ageing. The results presented are more focused on the oil-impregnated mock-ups with cold-pressed linseed oil since results have indicated that this causes more extended changes upon ageing.

Keywords: cold-pressed linseed oil; alkaline-refined linseed oil; stand oil; pure cellulosic paper; lignocellulosic paper; ATR-FTIR; reflectance FTIR



Citation: Banou, P.; Boyatzis, S.; Choulis, K.; Theodorakopoulos, C.; Alexopoulou, A. Oil Media on Paper: Investigating the Interaction of Cold-Pressed Linseed Oil with Paper Supports with FTIR Analysis.

Polymers **2023**, *15*, 2567. <https://doi.org/10.3390/polym15112567>

Academic Editors: Anamaria Irimia and Carmen-Mihaela Popescu

Received: 7 March 2023

Revised: 30 May 2023

Accepted: 31 May 2023

Published: 2 June 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Books, archival material, and works of art on paper present specific types of damage, when the oil binders in oil paints and traditional oil-based inks are absorbed by the paper supports, such as discolouration, loss of mechanical strength, and drop of pH. These problems have been recorded in diverse case studies, differing in intensity and extent, setting questions for the input of materials, paper, and oil type [1–5]. The combination of paper and oil could raise substantial concerns for the preservation of works upon ageing since the condition of the oiled areas of the support could deteriorate, and these could break into pieces, locally, but also overall [6].

As far as works of cultural heritage are concerned, only limited research on this matter has been reported until recently [7–10]. Although there is research on the effect of mineral oils used for the insulation of Kraft paper in transformers [11–15], the results could not be applied to printed material and works of art, where drying oil binders are used as oil binders. In addition, Kraft paper could not reflect the variety of paper supports used for works of art, archival material, and books.

Recently, the authors of this work have published results of the study on the changes in the optical, mechanical, and chemical properties that occur on the system of paper–linseed

oil upon ageing, aiming to the interpretation of damage recorded on works of art and printed materials due to oil-binder absorption [16,17]. The outcome of colourimetry, opacity, pH, and tensile strength measurements indicated that linseed oil has a predominant role in these changes, highlighting that the different linseed oil formulations and paper types have an input to the differences noted between the different sets of mock-ups. Transmittance Fourier-transform infrared spectroscopy (FTIR) analysis supported the results derived by the other methods of research and also indicated that the presence of linseed oil can induce the conditions to promote the deterioration of the oil-impregnated paper mock-ups upon ageing, as it has been suggested by the intense drop of pH of the oil-impregnated mock-ups from the initial stages of ageing and the reduction of the mechanical strength upon ageing. It also indicated that there were variations in the extent of oxidation and hydrolysis in the different series of mock-ups when the combinations of linseed oil formulations and paper types differ [16,17].

However, that work did not provide facts on the input of the three linseed oil formulations, or that of the paper content, on the chemical changes of the system of paper–linseed oil upon ageing, which is the aim of the present work. Therefore, the objective of the applied experimental methodology is to provide a hypothesis on the causes of the differences recorded between the various sets of mock-ups in their chemical behaviours, and, furthermore, their optical and mechanical changes of properties upon ageing. So, the results could contribute to the interpretation of the diversity in the condition recorded on the oiled areas of the supports of works of art, but also to the condition assessment of the category of oil media on paper.

The present work will focus on the results delivered by attenuated total reflectance (ATR) FTIR and reflectance FTIR analysis to complement those of transmittance FTIR. ATR-FTIR was conducted to investigate the chemical changes of the three linseed oil formulations individually, namely, that of cold-pressed linseed oil, alkaline-refined linseed oil, and stand oil, that submitted to the same accelerated ageing conditions as the oil-impregnated mock-ups (80 °C and 77% RH). In addition, reflectance FTIR was used to analyse the dried linseed oil films that were extracted from the oil-impregnated mock-ups. Since cold-pressed linseed oil presented similar changes to those of refined linseed oil, which were more extended than stand oil, the results on oil-impregnated paper mock-ups with cold-pressed linseed oil, made of three different types of paper, are discussed in comparison with those of neat linseed oil mock-ups and the oil films resulted from oil extraction (details of the products used are available in the Supplementary Materials Table S1).

A pure cellulosic and two lignocellulosic papers were used for the mock-ups to investigate whether the absence, removal, or presence of lignin content in the pulp has an effect on the system of paper–linseed oil. Although the presence of lignin has been regarded as responsible for the deterioration of the supports in the past, recent studies have indicated that although it causes the paper to be light-sensitive when it is present, it may act as a hindered phenolic antioxidant [18]. In addition, the function of the network of lignin molecules provides a mechanically strong composite material with cellulose fibres [19].

Finally, qualitative and quantitative processing of the results were performed to investigate the differences recorded upon ageing between the sets of oil-impregnated paper mock-ups.

2. Experimental

2.1. Materials

Three formulations of linseed oil and three types of paper support were used to prepare several series of mock-ups, employing standardised models prepared to serve the purposes of this study. Linseed oil was selected as the most representative oil binder used in printmaking and oil painting until the 19th century. The three types of linseed oil were selected that differ in the method of manufacture, namely, cold-pressed linseed oil (CP), alkaline-refined linseed oil (RF), and stand oil (StL). Cold-pressed linseed oil was selected as the purest type of linseed oil since it has not been subjected to a thermal or chemical

process; alkaline-refined linseed oil is the most commonly used type for oil painting, which is thermally and chemically processed during manufacture, and stand oil, which is pre-polymerised through long-term processing in high temperature in the presence or absence of air. The difference in the methodology of oil manufacture provides these formulations with different physicochemical properties, such as wetting power, drying rate, yellowing or darkening, viscosity, rheology, acid value, and degree of polymerization [20–25].

Mock-ups were made of pure cellulosic paper and two types of lignocellulosic papers (with different lignin content). In particular, the paper described as “Cotton” paper (C), is made of pure cotton linters, and it is unbuffered, with no fillers or sizing, 80 g/m². This paper type provides the purest form of paper. For the lignocellulosic papers, a typical watercolour paper, “Montval” (M) white colour, cold-pressed, acid-free, made of wood pulp (soft and hardwood fibres) and limited lignin content, without optical brighteners or additives, 185 g/m², and a wrapping paper, described as “Kraft” (K), brown colour, 100 g/m², buffered, made of soft and hardwood fibres, containing lignin, fillers, additives, and metallic contamination.

The pulp content (fibres, lignin, sizing, and additives) and the physical properties (colour, weight, and surface characteristics) of these papers responded to the characteristics of the supports recorded in original case studies of works presenting problematic oiled areas, and represent a vast majority of the papers used for the creation of works of art and printed material through time [9]. The use of lignocellulosic supports refers to the paper supports mostly used from the mid-19th century until today.

2.2. Preparation of Mock-Ups and Artificial Ageing

Paper strips, 2.5 × 10 cm (width × length), comprising the three paper types were cut for the preparation sets of mock-ups, for the series of plain papers and those of oil-impregnated ones. For the sets of oil-impregnated mock-ups, paper strips were impregnated with 0.3 mL of the three types of linseed oil, respectively, using a 1 mL syringe. The volume of oil was adequate for uniformly impregnating the paper strips of all types, without leaving excess.

After 40 days of air drying at room conditions of 22 °C and 52% RH, in the dark (stage of ageing 0/40, while the stage of ageing 0 indicates that the mock-ups have not been subjected to drying or any other process), the mock-ups were subjected to artificial ageing in the dark, with controlled conditions of 77% relative humidity (engaging saturated aqueous solution of sodium chloride, 0.15 g/mL) and temperature of 80 °C in airtight vessels for 2, 4, 7, 14, 21, and 28 days (Figure 1). This methodology is recommended by the Library of Congress preservation department for ageing papers involved in experimental procedures, and it has been used in previous relevant works [9,16–18,26]. To investigate the chemical changes of the three linseed oil formulations, 0.3 mL of each linseed oil formulation was applied on a glass vials slide, one for each ageing stage. These were submitted to the same ageing conditions as for the plain paper and oil-impregnated mock-ups. In total, 15 sets of mock-ups were prepared to serve the purposes of research, as presented in Table 1.

For the study of the possible interaction of the linseed oil and paper support upon ageing, after the end of artificial ageing, oil was extracted by the oil-impregnated paper strips using chloroform, and then both the solution and the paper were submitted to FTIR analysis. For oil extraction, a piece of the oil-impregnated mock-ups (size of 1 × 2 cm) was immersed in 1 mL of chloroform in a glass vial and then placed in an ultrasonic bath sonicator for 20 min.

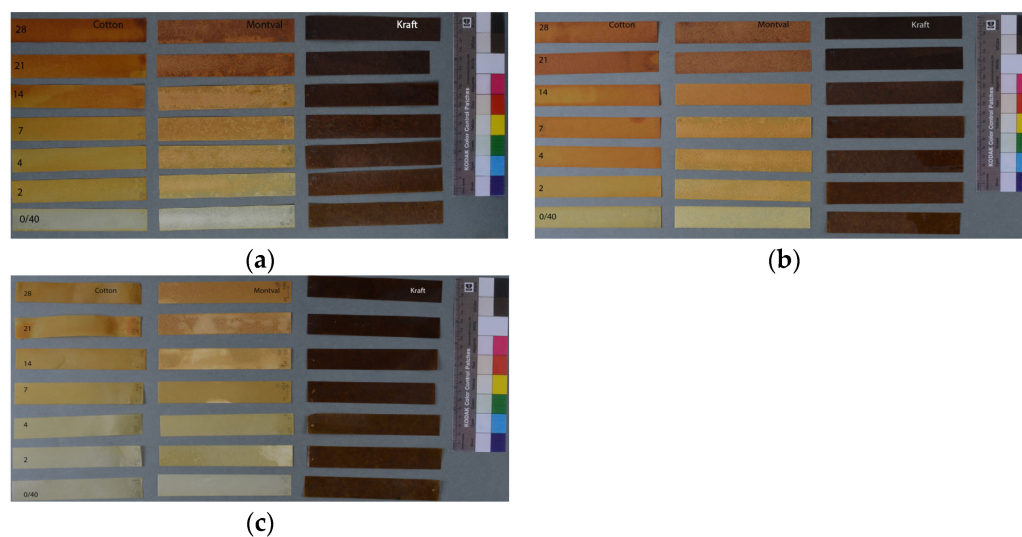


Figure 1. Sets of oil-impregnated mock-ups at the several stages of ageing (0/40, 2, 4, 7, 14, 21, and 28 days) of all paper types: (a) oil-impregnated mock-ups with cold-pressed linseed oil, (b) oil-impregnated mock-ups with refined linseed oil, and (c) oil-impregnated mock-ups with stand oil. Cotton mock-ups on the left, Montval mock-ups in the centre, and Kraft mock-ups on the right.

Table 1. The series of mock-ups and their symbols, respectively.

	Symbol	Materials
1	C	Plain Cotton paper
2	M	Plain Montval paper
3	K	Plain Kraft paper
4	CP	Cold-pressed linseed oil
5	RF	Refined linseed oil
6	StL	Stand oil
7	CCP	Cotton paper impregnated with cold-pressed linseed oil
8	CRF	Cotton paper impregnated with refined linseed oil
9	CStL	Cotton paper impregnated with stand oil
10	MCP	Montval paper impregnated with cold-pressed linseed oil
11	MRF	Montval paper impregnated with refined linseed oil
12	MStL	Montval paper impregnated with stand oil
13	KCP	Kraft paper impregnated with cold-pressed linseed oil
14	KRF	Kraft paper impregnated with refined linseed oil
15	KStL	Kraft paper impregnated with stand oil

2.3. Methodology

Analysis of oil mock-ups was performed on a Bruker Alpha II FT-IR equipped with a Bruker diamond crystal ATR spectrometer (manufacturer's spectral range $7500\text{--}400\text{ cm}^{-1}$), in absorbance mode, in the $4000\text{--}400\text{ cm}^{-1}$ region, at a resolution of 4 cm^{-1} , and by summing 24 scans. The spectra were recorded on Bruker OPUS v.8.5 software and they were further processed on Spectragryph v.1.2.16. Normalisation correction was applied in all spectra. Second-order derivative FTIR spectra were studied to resolve overlapping peaks in which molecular groups with carbonyl bands contributed within a wide wavenumber range from $1760\text{ to }1695\text{ cm}^{-1}$ and, in particular, the peaks at $c.1745\text{ cm}^{-1}$ due to carbonyls in glycerol ester linkages, and at $c.1709\text{ cm}^{-1}$ due to carbonyls in carboxylic

acid groups [26–30]. Second-derivative spectroscopy is a technique which enhances the separation of overlapping peaks of two or more components, a discrimination in favour of the sharpest features of a spectrum, and is used to eliminate interferences by broadband constituents [31,32].

For the ATR-FTIR analysis, the plain paper mock-ups (without the oil application) and the oil-impregnated paper mock-ups were placed directly on the diamond crystal (see the Supplementary Materials, Figure S1a). The neat linseed oil formulations were scraped off the glass surface with a scalpel 10A and placed on the ATR diamond crystal. For the fresh linseed oil formulations, a small droplet was applied to the diamond cell.

The performance of the analysis had to deal with the physical changes on the mock-ups upon ageing. At the first stages of ageing, an oil film covers the whole surface of the oil-impregnated mock-ups, while, in the core of the paper, the fibres and oil form a united mass. Gradually, the oil film becomes more “solid”, but it slowly recesses into the fibre net. After 14 days, the oil turns into a gel and movable form. Similar changes were recorded in the mock-ups of plain linseed oil formulations [16,17]. All these alterations imposed different variations in the application of the methodology (i.e., application of pressure).

Bruker Alpha II FT-IR was also used for reflectance FTIR. This was used only for the cold-pressed linseed oil extracted from oil-impregnated mock-ups. A droplet of the solution derived from the oil-extraction procedure was applied to a golden mirror substrate and allowed the solvent to evaporate. Analysis was conducted on the fine cold-pressed oil film formed on the golden mirror (transflectance) (see the Supplementary Materials, Figure S1b).

For all forms of analysis, and all series of mock-ups, measurements were taken from three different mock-ups at each ageing stage.

3. Results Discussion

Research work on this matter resulted in a plethora of results. Only the findings that strongly support the objectives of this work are presented. Supportive information on the results has been included in the Supplementary Materials. Please note that the tables and figures included in the Supplementary Materials bear the characteristic symbol S.

3.1. Plain Papers

ATR-FTIR analysis showed the profile of a pure cellulosic paper (cotton-based) for the “Cotton” paper and a typical lignocellulosic paper profile for “Montval” and “Kraft” papers, indicating the removal of lignin for “Montval”. The results were analogous to those delivered by transmittance FTIR analysis [16,17].

In particular, ATR-FTIR analysis of Cotton paper showed absorption at the band of 999 cm^{-1} , as well as the C-C ring breathing band at $\sim 1105\text{ cm}^{-1}$ and the C-O-C glycosidic ether at $\sim 1155\text{ cm}^{-1}$, which are assigned as fingerprints of cellulose in paper [27,33–39]. Other characteristic bands that presented absorption and are related to the chemical structure of cellulose were hydrogen-bonded OH stretching at around $3600\text{--}3000\text{ cm}^{-1}$, CH stretching at 2917 cm^{-1} , and CH wagging at 1316 cm^{-1} (Figure 2). The FTIR spectrum delivered was representative of cellulosic fibres, based on previous works (see Table S2).

ATR-FTIR analysis of Montval and Kraft paper showed a typical lignocellulosic paper profile (Figure 1). For the Kraft paper, the presence of wood pulp was indicated through the lignin absorption at about 1590 , 1505 , 1450 , ~ 1265 , ~ 900 , and 808 cm^{-1} , based on the results of previous works (Table S3). For the Montval paper, the removal of lignin was indicated by the lack of all lignin markers, while it showed characteristic absorption at $1202\text{--}1204$, 1050 , and 1030 cm^{-1} [27]. ATR-FTIR analysis, additionally, confirmed the presence of CaCO_3 in both papers by the marked absorptions at about 1430 and 874 cm^{-1} , along with clay, shown at $1030\text{--}1000$ and 910 cm^{-1} , typical of aluminum silicates [27] (Figure 2).

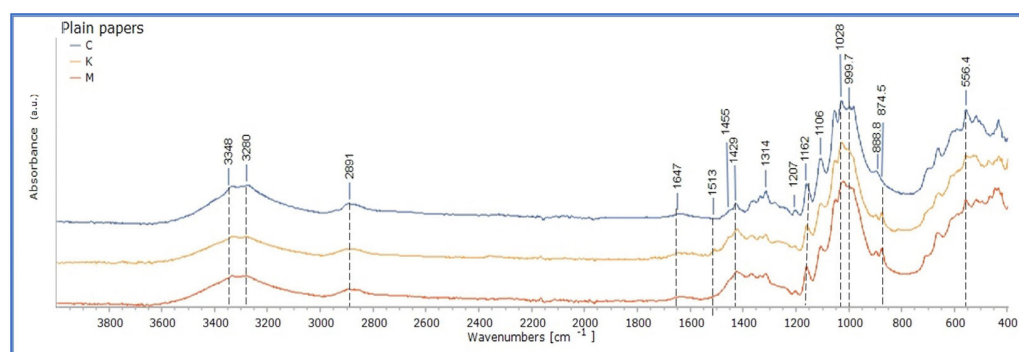


Figure 2. ATR-FTIR spectra of plain Cotton (C), Montval (M), and Kraft (K) mock-ups before ageing (stage 0).

ATR-FTIR spectra of plain Cotton, Montval, and Kraft mock-ups did not display notable changes upon ageing (0–28 days of ageing). This was evident in the presentation of ATR-FTIR spectra on an overlay form (see Figures S2–S4 in Supplementary Materials).

3.2. Neat Linseed Oil Formulations

The ATR-FTIR spectra of the fresh uncured cold-pressed linseed oil (CP) and refined linseed oil (RF) formulations (stage 0 days of ageing) were similar, showing the typical pattern of unsaturated triglycerols, which is typical for drying oils, and linseed oil respectively (see Table S4) [20,27]. The spectra of the CP and the RF appear to overlap completely (Figure 3). In this stage, no difference was recorded between the two formulations of linseed oil.

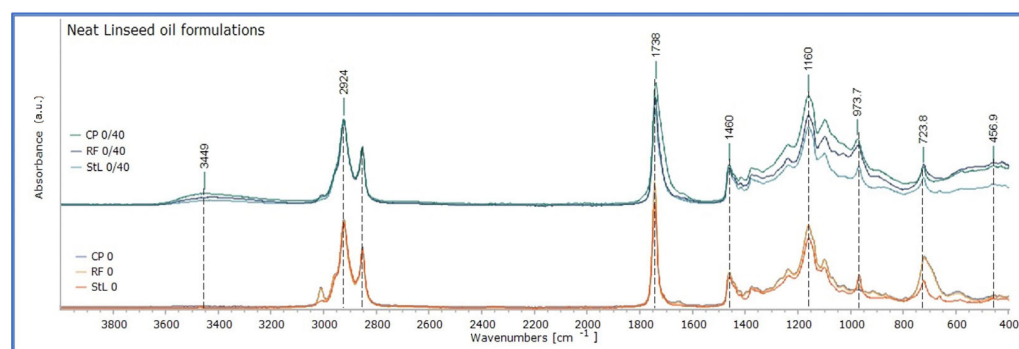


Figure 3. The FTIR spectra of the three linseed oil formulations (CP, RF, and StL), fresh and uncured on the lower part of the graph (0 days), and after 40 days of drying on the top part of the graphs (0–40 days).

In particular, they present absorption bands in the characteristic carbonyl band at 1746 cm^{-1} and the C–O stretching pattern at 1239, 1164, and 1101 cm^{-1} , which are diagnostic for triglyceride ester linkages. Also, the band of olefinic C–H stretching band at 3010 cm^{-1} is attributed exclusively to unconjugated, symmetrically disubstituted *cis* double bonds as expected for the fatty ester composition. There are also bands of the *cis* CH out-of-plane deformation at 722 cm^{-1} , the *cis* –HC–CH– stretching vibration at 1653 cm^{-1} , the CH deformations at $1000\text{--}800\text{ cm}^{-1}$, and the C–C stretching vibrations at $1680\text{--}1600\text{ cm}^{-1}$ [27].

The ATR-FTIR spectrum of the fresh and uncured stand oil (StL) was quite similar to those of CP and RF, since several bands overlap, as shown in Figure 3. However, the spectrum presented a comparatively lower absorption in the bands 3010 and 1653 cm^{-1} , which is commonly observed in the first stages of autoxidation (after an induction period) with the transformation of *cis*-to-*trans* double bonds, described as an isomerisation process [27]. This is consistent with the presence of an absorption band in 977 cm^{-1} , which reflects the

formation of *trans* C=C bonds. In addition, lower absorption with limited variations was observed in absorption between 1460 and 400 cm^{-1} (Figure 3), with a rather distinct one in the band of 723 cm^{-1} , that responds to *cis* (C-H) out-of-plane deformation [27,28]. The profile of the ATR-FTIR spectra responds more to that of saturated triglycerols (see Table S4), while the differences between StL, CP, and RF could be attributed to the extended heating in high temperatures of stand oil during manufacture, as suggested by other researchers [20].

Drying and hardening of linseed oil occur through the polymerization of triglycerides via autoxidation, a process involving free radicals. Free-radical polymerization reactions develop in three main stages, namely, the initiation, propagation, and termination, resulting in changes in the chemical structure of linseed oil [27,28,40]. However, polymerization competes with degradation processes, such as scission reactions, decomposition of unstable crosslinks, and hydrolysis [40].

After 40 days of drying in room conditions in the dark (stage 0/40 of ageing), ATR-FTIR spectra of the linseed oil formulations showed changes in absorption bands, as shown in Figure 3. It should be mentioned that the oil films of the three linseed oil formulations were already touch dry. The spectra of the three linseed oil formulations presented a comparable pattern of absorption, with variations in intensity. There were lower absorptions for CP and RF in the band of 3010 cm^{-1} , broadening of the band 1743 towards 1700 cm^{-1} , and an increase in absorptions of between 1350 and 700 cm^{-1} . These reflect the initial chemical reactions involved in the drying of fresh linseed oil, mainly due to autoxidation, involving cross-linking reactions taking place between the triacylglycerols [18,26,27]. Due to these changes, the absorption spectra of the three linseed oil formulations became similar, with those of RF and StL overlapping in the region 3100–1375 cm^{-1} (Figure 3). Comparatively, cold-pressed oil appeared to have more intense changes between 0 and 40 days of drying, while variations for stand oil were more limited, as shown in Figures 3 and 4. It could be suggested that the absence of heat and chemical pre-treatment of cold-pressed linseed oil, induced a more intense chemical condition. On the other hand, pre-polymerisation processing of stand oil has as a result lower absorption of oxygen, thus, slower development of oxidation reactions [21]. This observation was supported by the calculation of the integral ratio of the derivatives bands 1820–1570 cm^{-1} and 1450–400 cm^{-1} of the fresh linseed oil formulations dried for 40 days by those freshly applied, which presented the most characteristic changes upon ageing, and they are associated with the oxidative degradation and polymerization of oils (see Tables 2 and S5).

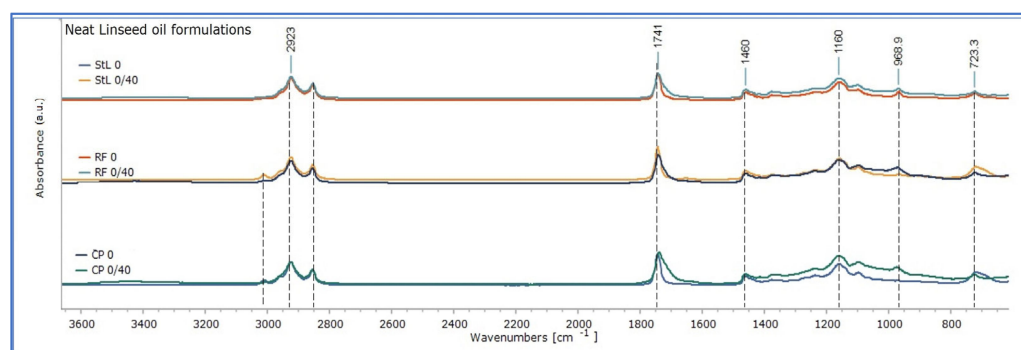


Figure 4. The FTIR spectra of the three linseed oil formulations, fresh and uncured, and after 40 days of drying, in sets for each formulation. On the top, cold-pressed linseed oil (CP), in the middle alkaline-refined linseed oil (RF), and at the bottom, stand oil (StL).

Table 2. Calculation of the integral ratio of two different absorption bands of the three linseed oil formulations after drying for 40 days by those in fresh form.

Absorption Band (cm^{-1})	CP 0–40/CP 0	RF 0–40/RF 0	StL 0–40/StL 0
1820–1570	2.03	1.42	1.57
1450–400	2.95	1.58	3.14

Upon ageing of the three linseed oil formulations, CP, again, presented the most intense changes (Figure 5). These developed with a gradual broadening of the band up to the 7th day of ageing, while on the 14th day of ageing the peak of 1738 cm^{-1} and that of 1710 cm^{-1} were equal, and, at the final stages, the peak of 1710 cm^{-1} was increased to a higher level than the peak at 1738 cm^{-1} . Broadening of the specific band indicates the formation of carbonyl-containing species, such as aldehydes, ketones, and carboxylic acids, that occur during oxidative polymerisation, while the increase in absorption at the peak of 1710 cm^{-1} corresponds to the formation of carboxylic groups, thus acids, indicating the hydrolysis of the oil after the 14th day of ageing [20,27,28,40–42]. The development of these peaks was clearly observed after 28 days of ageing in the derivatives of the band $1760\text{--}1710\text{ cm}^{-1}$ (Figures 6 and S5).

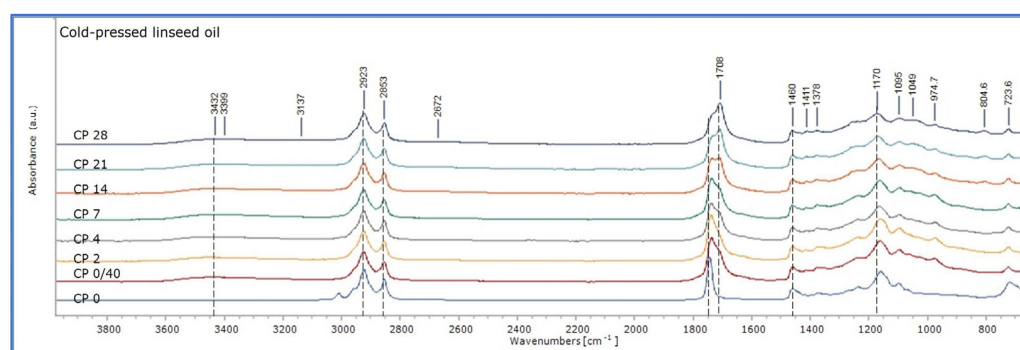


Figure 5. ATR-FTIR spectra of cold-pressed linseed oil mock-ups (CP) at all ageing stages (0–28 days of ageing).

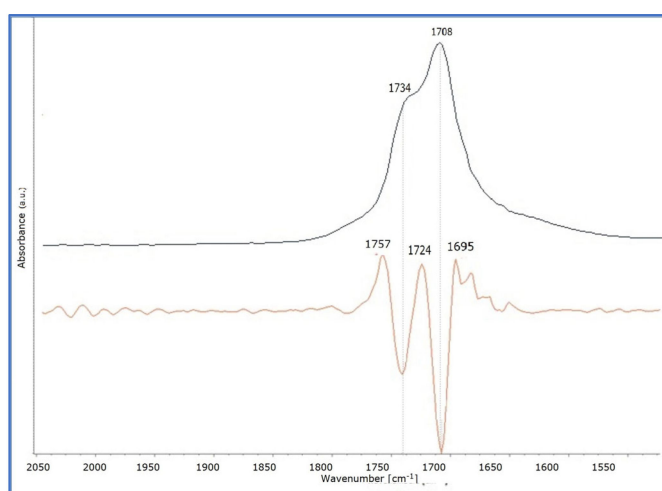


Figure 6. The ATR-FTIR spectra of CP at 28 days of ageing (on the top, blue line) and the derivatives (at the bottom, yellowish line). The development of two different peaks with the band of $1760\text{--}1700\text{ cm}^{-1}$ at 1738 and 1708 cm^{-1} is observed.

RF mock-ups presented equivalent changes (Figure 7). It could be only suggested that they were slightly more intense in the final stages due to the broadening of the band $1760\text{--}1696\text{ cm}^{-1}$. Finally, for StL, these changes developed at a more limited extent, so those recorded in the spectrum of the 28th day of ageing corresponded to those of the 14th day of ageing for the other two oil formulations (Figure 8).

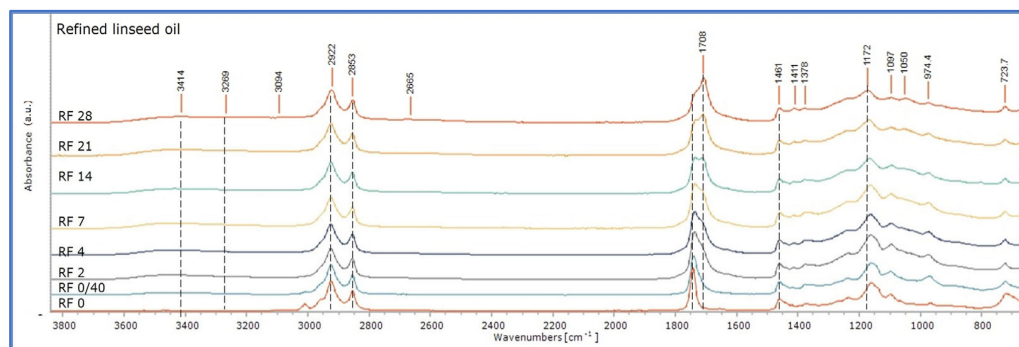


Figure 7. ATR-FTIR spectra of refined linseed oil mock-ups (RF) at all ageing stages (0–28 days of ageing).

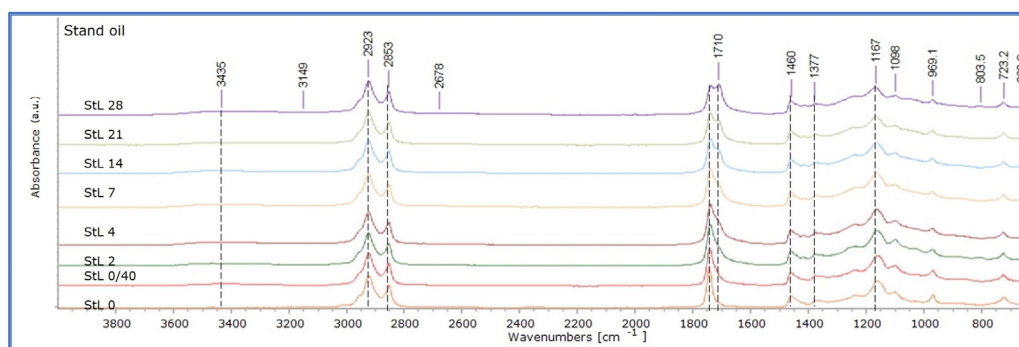


Figure 8. ATR-FTIR stand oil mock-ups (StL) at all ageing stages (0–28 days of ageing).

The development of oxidative degradation, and the possible differences between the linseed oil formulations, were studied by calculating the ratio of the integration of the band $1900\text{--}1550\text{ cm}^{-1}$ by that of the hydrocarbons band $3200\text{--}2800\text{ cm}^{-1}$ (see Table S6 and Figure 9), following similar practices used by other authors to indicate the oxidation status of the oil films [31]. These results indicated that more intense changes occur at the first stages of ageing, and CP and RF present a similar trend, while the changes for StL were more subtle throughout ageing (Figure 9).

Additionally, the difference in the increase in absorption at 1710 cm^{-1} was studied by calculating the ratio of integration of the band $1730\text{--}1695\text{ cm}^{-1}$ by that of $1760\text{--}1730\text{ cm}^{-1}$ (see Table S7). The graphic representation of the results confirmed the aforementioned observations (Figure 10).

Since CP and RF presented similar changes upon ageing, and much more extended in comparison with StL, the interpretation of the results was focused on the mock-ups impregnated with cold-pressed linseed oil, which are presented in the following sections.

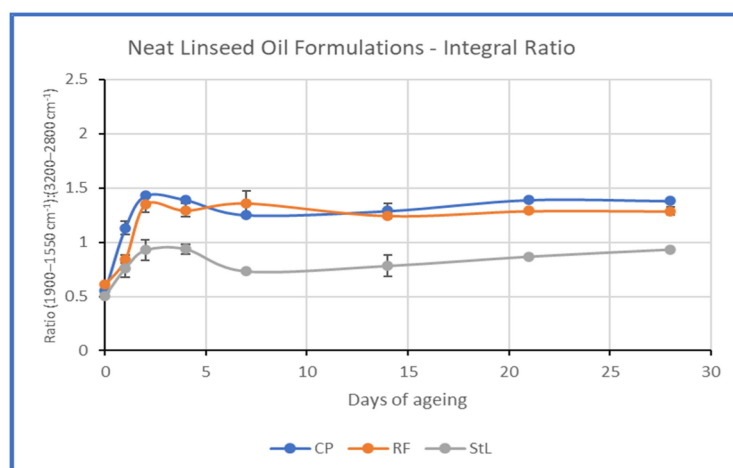


Figure 9. Graphic representation of the integral ratio of the band 1900–1550 cm^{-1} by that of the hydrocarbons' band 3200–2800 cm^{-1} .

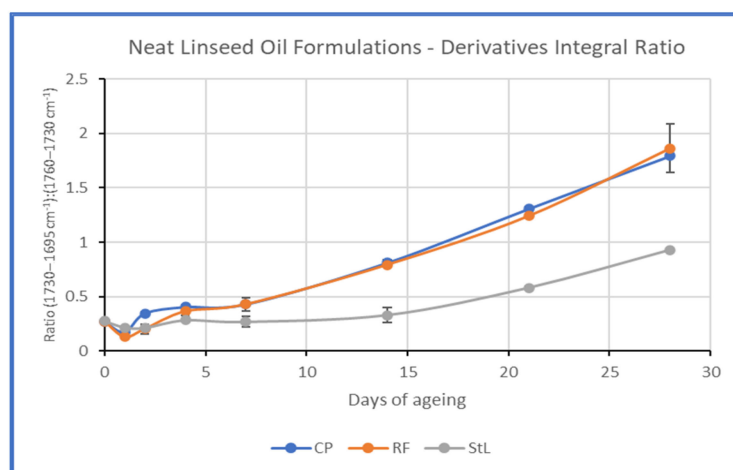


Figure 10. Graphic representation of the integral ratio of the band 1730–1695 cm^{-1} by that of 1760–1730 cm^{-1} .

3.3. Cold-Pressed Oil Extractions

The reflection-FTIR spectra of CP extracted from the Cotton oil-impregnated mock-ups (CP/C) presented the most significant changes on the band 1700–1650 cm^{-1} at all stages of ageing. The spectrum of the extracted CP from the oil-impregnated mock-up after 40 days of drying (stage 0/40) indicated that the autoxidation had already been initiated, taking into consideration the broadening of the band between 1750–1700 cm^{-1} . There were limited changes up to the 21st and 28th day of ageing, where the peak at 1710 cm^{-1} appeared to increase higher than that of 1741 cm^{-1} , indicating the hydrolytic and oxidative degradation of the CP (see Figures 11a and S6). From 0 to 14 days of ageing a peak at 1720 cm^{-1} was also recorded, possibly indicating the formation of saturated ketones, which was not evident in the analysis of neat linseed oil formulations. Likewise, a constant but limited noise was recorded between 1700 and 1450 cm^{-1} .

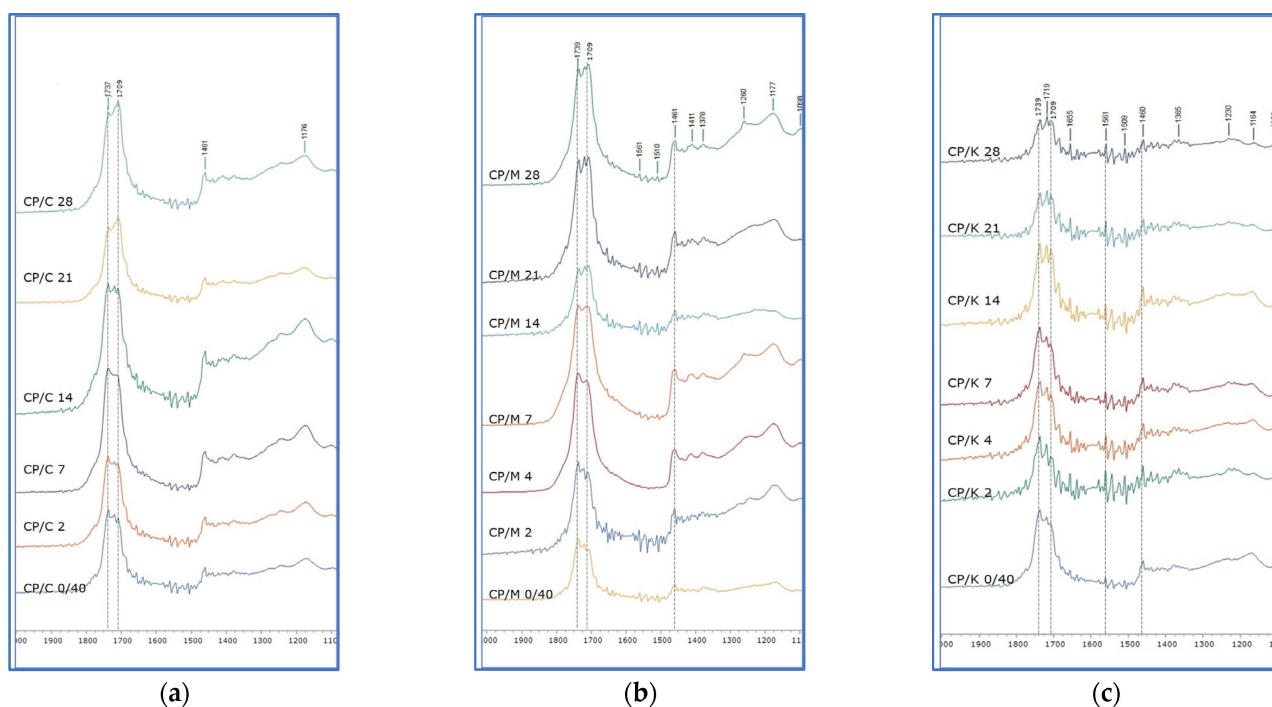


Figure 11. The reflection-FTIR spectra of CP extraction from (a) Cotton oil-impregnated mock-ups, (b) Montval oil-impregnated mock-ups, and (c) Kraft oil-impregnated mock-ups, upon ageing.

The reflectance spectra of the CP extracted from Montval oil-impregnated mock-ups (CP/M) at the several stages of ageing presented differences between that of CP extracted from Cotton oil-impregnated mock-ups. Again, the most significant changes were recorded between $1750\text{--}1710\text{ cm}^{-1}$. Although there is a broadening of the region, the band at the 1710 cm^{-1} increased, but it only reaches slightly higher than that of 1738 cm^{-1} (Figures 11b and S7). There were also peaks between 1735 and 1710 cm^{-1} , almost at the same level. Also, there was an intense “noise” between $1700\text{--}1462\text{ cm}^{-1}$. All these extra peaks indicate the development of chemical actions that did not occur in neat linseed oil formulations. It could be suggested that CP have reacted with the pulp content materials, such as the calcium ions (Ca^{+2}) ($\text{Ca}(\text{OH})_2$ is used in the paper-making process) providing a slightly diverse chemical profile. It could be suggested that the peaks responded to the presence of fatty acid metal soap. Fatty acid metal soap formation on the painting layers of oil paintings on canvas, and their effect on their preservation, is a known research issue [43–50]. Metal soap formation occurs during the neutralisation of the fatty acids produced by the hydrolytic degradation of oil binders, when the latter react with metal ions in metal hydroxides, oxides, and mixed hydroxide salts, creating an ionomeric-like structure [27,43,44]. Calcium fatty soaps have been identified, among others, in previous works [27,43,51]. Further work is needed to investigate the formation of possible by-products due to the reaction of linseed oil and paper pulp contents.

Similar observations were made for CP extracted from Kraft oil-impregnated mock-ups (CP/K). In this case, the peaks in 1719 and 1708 cm^{-1} reached the same level as that at 1739 cm^{-1} (Figures 11c and S8). Detail images and the derivatives of the band of $1700\text{--}1650\text{ cm}^{-1}$ confirmed the formation of a separate peak at 1720 cm^{-1} , but also of others, presenting a different degree of absorption intensity among the sets of impregnated mock-ups (Figures 12 and S9).

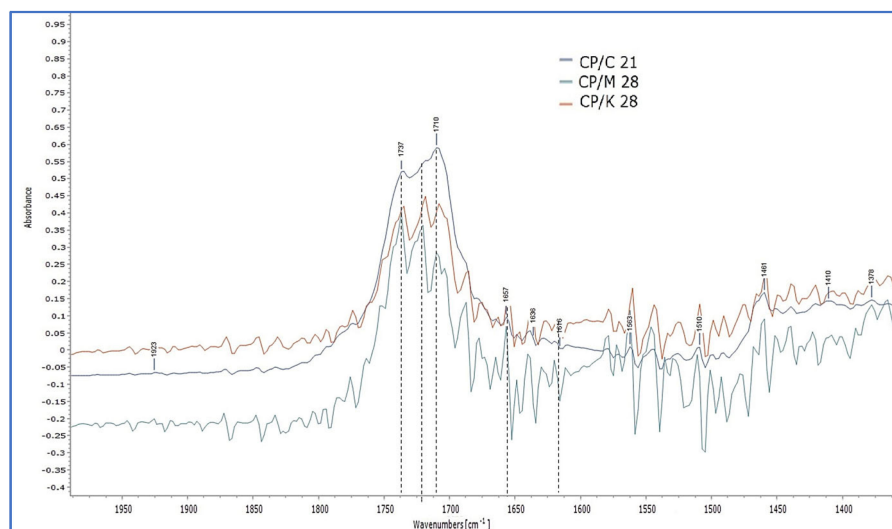


Figure 12. Detail image of the CPs reflection spectra derived from the extraction of C, M, and K impregnated mock-ups, at the final stage of ageing. The formation of several peaks on the band 1700–1550 cm^{-1} is evident.

The results provided initial indications that paper, and, in particular, pulp content, has an input to the development of chemical changes in the system paper–linseed oil. This hypothesis could provide explanations for the differences recorded in spectra of CP derived from the extraction of different paper-type impregnated mock-ups. It should not be ignored the lack of alkaline buffer in Cotton’s paper pulp and the presence of lignin, but also of impurities (such as traces of metals) in Kraft’s one. The presence of an alkaline buffer, and, possibly, that of lignin, in the paper pulp, could restrain the production of acids or could induce variant conditions for the evolution of other chemical reactions and by-products, consequently.

3.4. Oil-Impregnated Mock-Ups

The spectra of Cotton mock-ups impregnated with CP presented more characteristic changes in the bands that respond to carbonyl-containing species (such as aldehydes and ketones) and carboxyl acids (1600–1750 cm^{-1}), which are associated both with cellulose oxidation as well as the oxidation of linseed oil [27,28,35–42]. Even at stage 0 (after 40 days of drying), the broadening of the band 1750–1600 cm^{-1} , suggests that the system was in an oxidated stage (Figure 13). This implies that the application of CP even on the purest form of paper could promote oxidation reactions in the system of paper–linseed oil within 40 days. This can be attributed to the oxidative degradation of linseed oil that provides the right conditions for the oxidation of cellulose or the oxidation of the system paper–linseed oil. This band presented a gradual increase in absorption upon ageing. After seven days of ageing, the absorption at the peak of 1710 cm^{-1} increased higher than that of 1735 cm^{-1} , implying conditions of deterioration of the system paper–oil (Figure 13). It could be suggested that the lack of sizing, alkaline buffer, or other additives allowed the cold-pressed linseed oil to be thoroughly introduced to the fibre net and, possibly, in duced chemical reactions in the system without having any factor to restrain them. The results have confirmed the dramatic decrease in the tensile strength of the Cotton oil-impregnated mock-ups with CP upon ageing [16].

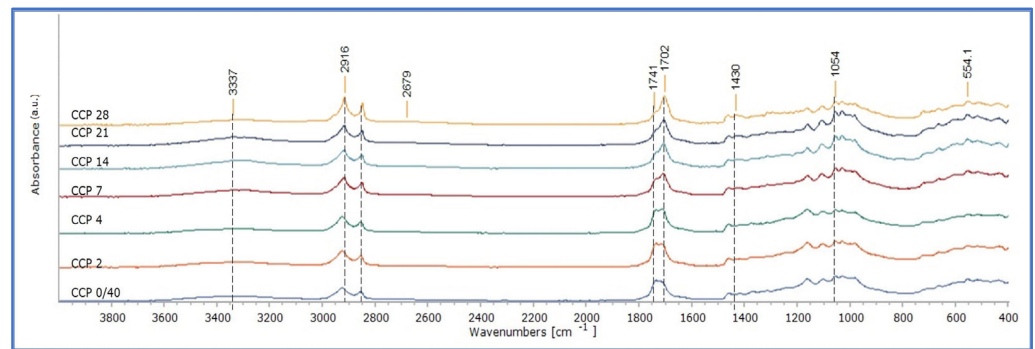


Figure 13. ATR-FTIR spectra of Cotton impregnated mock-ups with cold-pressed linseed oil (CCP).

Montval and Kraft oil-impregnated mock-ups presented similar behaviour with those of Cotton at the first stages of ageing, but the increase in absorption in the band $1750\text{--}1600\text{ cm}^{-1}$ appears to be less intense. Also, the increase in absorption at 1710 cm^{-1} is more limited, as it did not reach higher than that of 1738 cm^{-1} for the Montval mock-ups at the final stages of ageing, while the same one appeared to be slightly higher for the Kraft mock-ups (Figures 14 and 15). These observations were supported by the calculation of the integral ratio of the band $1730\text{--}1695\text{ cm}^{-1}$ by that of $1760\text{--}1730\text{ cm}^{-1}$ (Figure 16, Table S8). It could be suggested that the Montval and Kraft mock-ups did not reach the same stage of deterioration as those of Cotton. This hypothesis could also support the results of tensile strength measurements that showed lesser mechanical-strength reduction for Montval and Kraft oil-impregnated mock-ups [16].

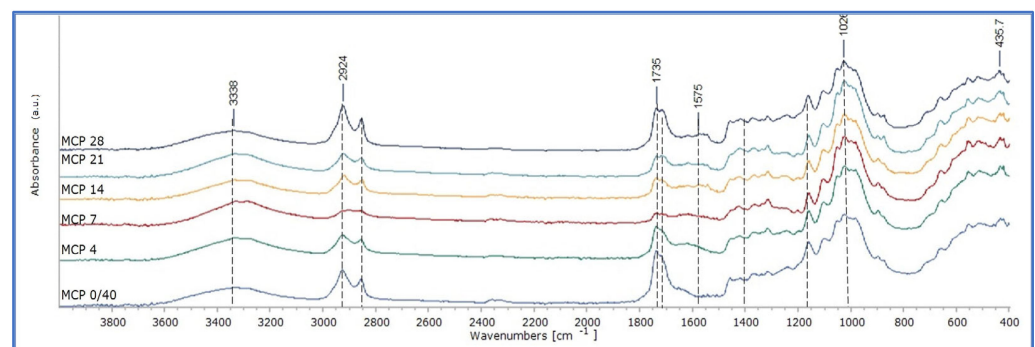


Figure 14. ATR-FTIR spectra of Montval impregnated mock-ups with cold-pressed linseed oil (MCP).

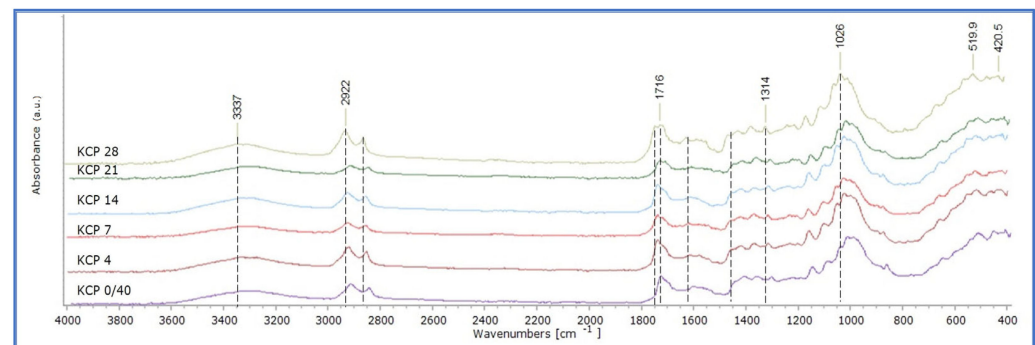


Figure 15. ATR-FTIR spectra of Kraft impregnated mock-ups with cold-pressed linseed oil (KCP).

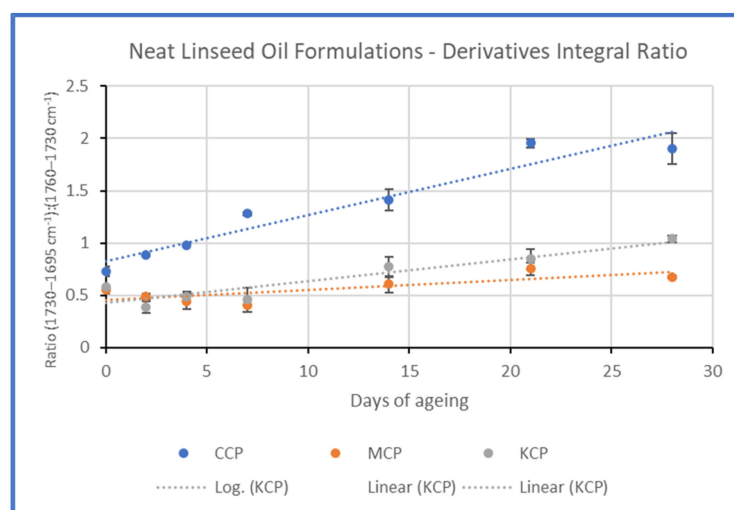
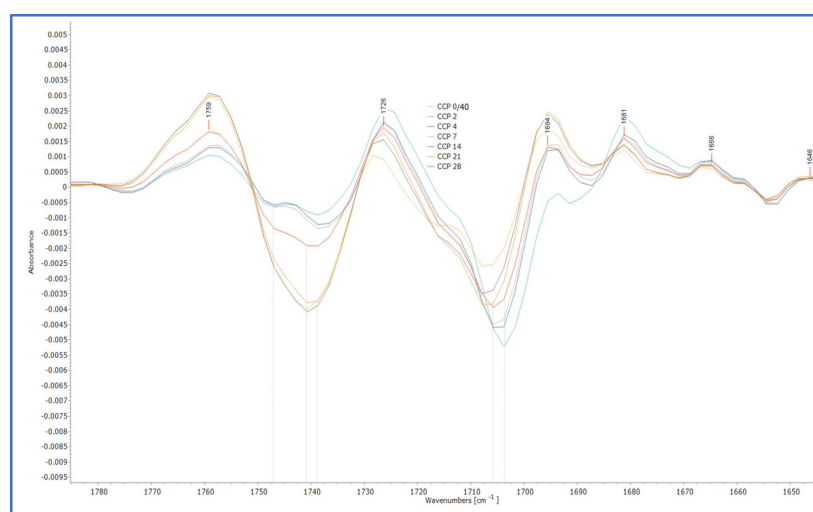


Figure 16. Graphic representation of the calculation of the integral ratio of the band $1730\text{--}1695\text{ cm}^{-1}$ by that of $1760\text{--}1730\text{ cm}^{-1}$. The trendlines showed the increase in the band $1730\text{--}1695\text{ cm}^{-1}$ was higher for Cotton mock-ups, followed by Kraft, and then by Montval at a lower degree.

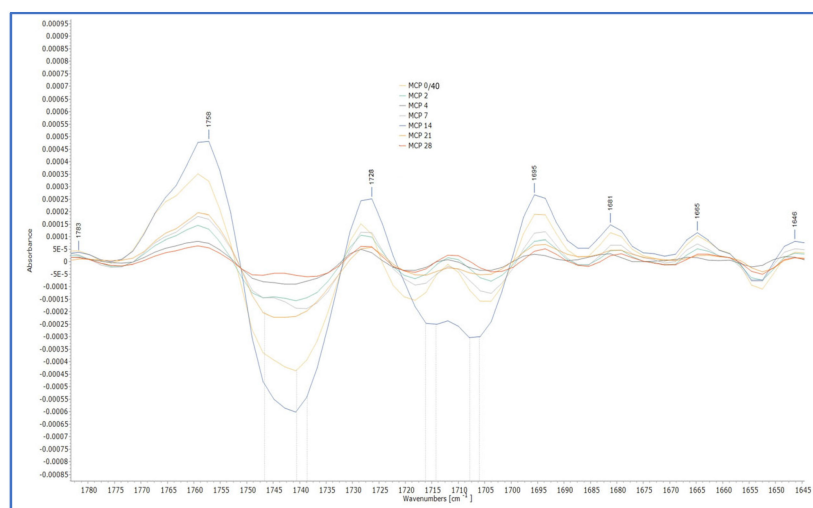
However, Montval and Kraft oil-impregnated mock-ups showed the evolution of an absorption band at $1650\text{--}1540\text{ cm}^{-1}$, which was more evident at the final stages of ageing. This could be attributed to the formation of carboxylates or fatty acid metal soaps, such as calcium or aluminum soaps, formulated by the reaction of free fatty acids with the compounds of the alkaline buffer and additives in the paper pulp. This could explain the lower absorption of the peak at 1710 cm^{-1} at the final stages of ageing, in comparison to that of the neat cold-pressed linseed oil, since fatty acids were possibly consumed for the soap formulation.

For all sets of mock-ups studied in the present work, ATR-FTIR spectra did not provide clear indications for the changes that occur to other bands upon ageing. Transmittance FTIR has indicated reduction for the bands that respond to volatile oxidation compounds ($2855\text{--}2853\text{ cm}^{-1}$ and 2810 cm^{-1}), hydroperoxides, and alcohols ($3200\text{--}3600\text{ cm}^{-1}$ and $1100\text{--}1210\text{ cm}^{-1}$), and the formation of conjugated bonds (such as in 1624 , 1633 , 950 , and 723 cm^{-1}) and oxidative polymerization ($1099\text{--}1238\text{ cm}^{-1}$) in the final stages of ageing. All these could be attributed to the degradation of linseed oil according to the FTIR analysis of linseed oil subjected to different accelerating and storage conditions reported by other researchers [27–30].

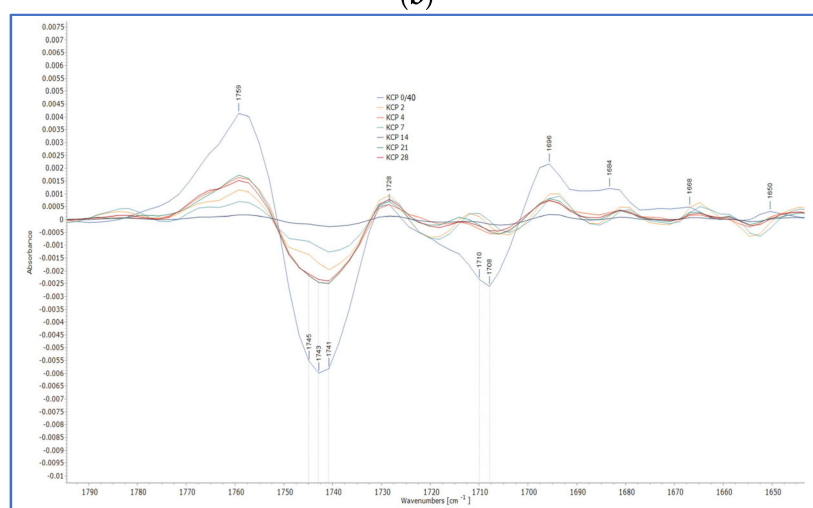
The spectra of the oil-impregnated mock-ups were compared with those of the plain papers, the neat linseed oil formulations, and those derived from oil extraction. It was evident that CP had the dominant effect on the evolution of chemical changes. However, more similarities in the evolution of chemical changes were observed between the oil-impregnated mock-ups with CP and those of CP extracted from the three types of papers, respectively. It could be suggested that the evolution of the absorption band $1650\text{--}1450\text{ cm}^{-1}$ on the spectra of oil-impregnated mock-ups possibly responds to the noise recorded on the band $1650\text{--}1450\text{ cm}^{-1}$ of the spectra derived from extracted CP from Montval and Kraft oil-impregnated mock-ups, possibly due to the same provenance, the presence of alkaline buffer, and other additives. Finally, the derivatives on the band $1745\text{--}1740\text{ cm}^{-1}$ for all sets of oil-impregnated mock-ups also showed the formation of a peak at 1720 cm^{-1} , recorded in oil-extraction spectra, presenting different absorption intensities. Two separate peaks were also recorded in the band of $1745\text{--}1730\text{ cm}^{-1}$ for Cotton and Montval oil-impregnated mock-ups in 1747 and 1738 cm^{-1} (Figure 17).



(a)



(b)



(c)

Figure 17. The second derivatives on the band $1750\text{--}1700\text{ cm}^{-1}$ for all oil-impregnated mock-ups, at all ageing stages: (a) Cotton oil-impregnated mock-ups with CP; (b) Montval oil-impregnated mock-ups with CP; and (c) Kraft oil-impregnated mock-ups with CP.

3.5. Paper after Oil Extraction

Oil extraction from oil-impregnated mock-ups required repeated extractions with chloroform to provide samples without residues of CP. Cotton oil-impregnated mock-ups presented the most extended chemical changes in comparison to those of Montval and Kraft, which follows with the aforementioned results, so these were selected to demonstrate the chemical changes of the paper support after oil extraction.

The Cotton paper mock-ups, after CP oil extraction, presented mostly changes in the carbonyl-containing band ($1740\text{--}700\text{ cm}^{-1}$). From the 4th day of ageing and onwards, a gradual increase in absorption on the band between $1700\text{--}1750\text{ cm}^{-1}$ was recorded, indicating the development of the oxidation of paper, while on the 21st day of ageing, the absorption at 1710 cm^{-1} increased and appeared to give a higher peak than the rest of the band (Figure 18). These changes could be attributed to the oxidation and oxidative hydrolysis of cellulose according to other researchers' results [52,53]. The hydrolysis of CP and the consequent formation of fatty acids created the conditions for the development of these chemical changes.

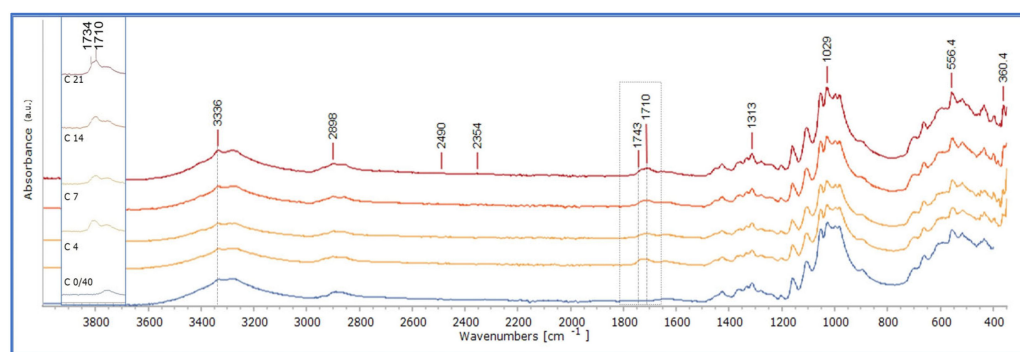


Figure 18. ATR-FTIR spectra of Cotton paper after cold-pressed linseed oil extraction on various stages of artificial ageing (0/40, 4, 7, 14, and 21 days, arrayed from the bottom to the top) and detail.

4. Conclusions

This work aimed to investigate the input of the different linseed oil formulations and paper types to the chemical changes that occur to the oil-impregnated mock-ups upon ageing and possible interactions between linseed oil and paper content that could influence their development.

Results showed that linseed oil is the dominating factor in the evolution of chemical reactions upon ageing. The results indicated that the most significant changes appear in the band $1750\text{ to }1700\text{ cm}^{-1}$. The ATR-FTIR of neat cold-pressed and alkaline-refined linseed oil presented similar changes upon ageing, much more extended in comparison with those recorded for stand oil. The process of manufacturing alkaline-refined linseed oil has a limited effect on the oxidative polymerization and degradation of the oil upon ageing. Pre-polymerisation of stand oil has a significant effect on the chemical changes upon ageing. Hence, the chemical changes of the paper–linseed oil system could be associated with the extent of those occurring to the linseed oil formulations, respectively. This has been indicated by the results obtained from the measurement of optical and mechanical properties in previous work by the authors [16,17].

However, it was the results of the cold-pressed linseed oil extracted from the oil-impregnated paper mock-ups that indicated that the paper pulp content has an input to the development of chemical reactions. These results also supported the interpretation of those derived from the oil-impregnated cotton mock-ups that presented common changes in certain areas of the FTIR spectra. It has been suggested that the presence of alkaline buffer in the paper pulp, possibly, constrains the formation of acids, that are, possibly, consumed to formulate metal soaps of fatty acids. The outcome of this work provides additional data for the variations in the extent of deterioration of oil-impregnated papers for the first time.

The results could not provide a secure hypothesis of the input of lignin to the chemical changes. Both lignocellulosic papers bear an alkaline reserve, so they present fewer extended chemical changes than oil-impregnated pure cellulosic paper. However, the oxidation of oil-impregnated Montval paper, in which lignin has been removed, appears to be even less than that of Kraft, which included lignin in its pulp content. Nevertheless, the additives and impurities in Kraft's pulp content could also have an input in that.

Thus, the applied methodology managed to complement previous results on the factors that influence the condition of the oiled areas of the support of archival and printed material, books, and works of art on paper.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/polym15112567/s1>, Table S1: Description of the materials used for the preparation of mock-ups, as provided by their manufacturers; Table S2: Characteristic infrared absorption bands for cellulosic fibres; Table S3: Characteristic infrared absorption bands for lignocellulosic papers; Table S4: Common vibrations in triacylglycerols; Table S5: Neat linseed oil formulations at 0 days of ageing and after 40 days of air drying: integral calculations; Table S6: Neat linseed oil formulations: Ratio of integrals (1900–1550 cm^{−1}): (3200–2800 cm^{−1}); Table S7: Neat linseed oil formulations: Ratio of derivatives' integrals (1730–1695 cm^{−1}): (1760–1730 cm^{−1}); Table S8: Oil-impregnated mock-ups: Ratio of derivatives integrals (1730–1695 cm^{−1}): (1760–1730 cm^{−1}); Figure S1: Images of the FTIR methodology used for the different types of analysis: (a) the set-up for the ATR-FTIR analysis for plain paper and oil-impregnated mock-ups, and (b) the set-up for Reflectance FTIR for the oil films derived from the oil extraction of the oil-impregnated mock-ups; Figure S2: ATR-FTIR spectra of plain Cotton (C) mock-ups at all stages of artificial ageing (0–28 days), in an overlay display; Figure S3: ATR-FTIR spectra of plain Montval (M) mock-ups at all stages of artificial ageing (0–28 days), in an overlay display; Figure S4: ATR-FTIR spectra of plain Kraft (K) mock-ups at all stages of artificial ageing (0–28 days), in an overlay display; Figure S5: The derivatives of the CP spectra at all ageing stages, on the band 1760–1700 cm^{−1}; Figure S6: The reflection-FTIR spectra of CP extraction from Cotton oil-impregnated mock-ups upon ageing; Figure S7: The reflection-FTIR spectra of CP extraction from Montval oil-impregnated mock-ups upon ageing; Figure S8: The reflection-FTIR spectra of CP extraction from Kraft oil-impregnated mock-ups upon ageing; Figure S9: Detail image of the derivatives of CPs reflection spectra that derived from the extraction of C, M, and K oil-impregnated mock-ups, at the final stage of ageing. The formation of several peaks on the band 1700–1550 cm^{−1} is clear.

Author Contributions: Conceptualization, P.B. and S.B.; methodology, P.B. and S.B.; software, P.B., S.B. and C.T.; validation, P.B. and S.B.; formal analysis, P.B.; investigation, P.B.; resources, P.B.; data curation, P.B.; writing—original draft preparation, P.B.; writing—review and editing, P.B.; visualization, P.B., S.B. and C.T.; supervision, A.A., K.C. and S.B. All authors have read and agreed to the published version of the manuscript.

Funding: Special Account for Research Grants of the University of West Attica (Greece) funded the publication of this article.

Institutional Review Board Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available yet as they derived from an ongoing PhD research project.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Engram, C. Oil painting on paper and board supports. *AICCM Bull.* **1991**, *17*, 13–20. [[CrossRef](#)]
2. James, C.; Corrigan, C.; Enshaian, M.C.; Greca, M.R. *Old Master Prints and Drawings*; University Press: Amsterdam, The Netherlands, 1997.
3. McAusland, J. Problems with works of art in oil on paper and their support: A paper conservator's viewpoint. In *General Meeting of the Association of British Picture Restorers*; Association of British Pictures Restorers: London, UK, 1989; pp. 1–6.
4. Kosek, J.; Green, L.R. A survey of oil paintings and sketches on paper in the collection in the British Museum: An assessment of stability. In *The IPC: Conference Papers Manchester*; Institute of Paper Conservation: London, UK, 1992; pp. 96–102.

5. Millard, T.; Le Cornu, E.; Smith, R.; Hasler, E.; Cowdy, H.; Chisholm, R.; King, E. The conservation of 830 oil paintings on paper by Marianne North. *J. Inst. Conserv.* **2011**, *34*, 159–172. [\[CrossRef\]](#)
6. Banou, P.; Alexopoulou, A.; Singer, B.W. The Treatment of Oil Paintings on Paper Supports Considerations on the Treatment Applications Used from the Past until the Present. *J. Pap. Conserv.* **2015**, *16*, 29–36. [\[CrossRef\]](#)
7. Daniels, V. Oxidative Damage and the Preservation of Organic Artefacts. *Free. Radic. Res. Commun.* **1989**, *5*, 213–220. [\[CrossRef\]](#) [\[PubMed\]](#)
8. Daniels, V. The discolouration of paper on ageing. *Pap. Conserv.* **1988**, *12*, 93–100. [\[CrossRef\]](#)
9. Banou, P.; Alexopoulou, A.; Chranioti, C.; Tsimogiannis, D.; Terlix, A.V.; Zervos, S.; Singer, B.W. The effect of oil binders on paper supports via VOC analysis. *J. Cult. Herit.* **2016**, *20*, 589–598. [\[CrossRef\]](#)
10. Elfecky, O.M.; Hassan, M.L. Artificial Aging and Deterioration of Oil-Painted Fabriano Paper and Cardboard Paper Supports. *J. Appl. Polym. Sci.* **2008**, *109*, 1594–1603. [\[CrossRef\]](#)
11. Emsley, A.M. The kinetics and mechanisms of degradation of cellulosic insulation in power transformers. *Polym. Degrad. Stab.* **1994**, *44*, 343–349. [\[CrossRef\]](#)
12. Hussaian Basha, C.H.; Mariprasath, T.; Kiran, S.R.; Murali, M. An experimental analysis of degradation of cellulosic insulating material immersed in natural ester oil for transformer. *ECS Trans* **2022**, *107*, 18957. [\[CrossRef\]](#)
13. Munajad, A.; Subroto, C.; Suwarno, H. Fourier transform infrared spectroscopy (FTIR) analysis of transformer insulation paper in natural ester. In Proceedings of the International Conference on High Voltage Engineering and Power Systems, Denpasar, Bali, 2–5 October 2017; pp. 446–450. [\[CrossRef\]](#)
14. Sun, P.; Sima, W.; Yang, M.; Wu, J. Influence of Thermal Aging on the Breakdown Characteristic of Transformer Oil Impregnated Paper. *IEEE Trans. Dielectr. Electr. Insul.* **2016**, *23*, 3373–3381. [\[CrossRef\]](#)
15. Suwarno, H.; Pasaribu, R.A. Thermal Aging of Mineral Oil-Paper Composite Insulation for High Voltage Transformer. *Int. J. Electr. Eng. Inform.* **2016**, *8*, 820–835. [\[CrossRef\]](#)
16. Banou, P.; Choulis, K.; Karabotsos, T.; Tsimogiannis, D.; Tsakanika, L.-A.; Tzia, C.; Alexopoulou, A. Oil Media on Paper: Investigating the Effect of Linseed Oils on Pure Cellulosic Paper Supports. A Research Matter of Damage Assessment. *Analytica* **2022**, *3*, 120–134. [\[CrossRef\]](#)
17. Banou, P.; Boyatzis, S.; Choulis, K.; Karabotsos, T.; Tsimogiannis, D.; Tsakanika, L.-A.; Tzia, C.; Alexopoulou, A. Oil Media on Paper: Investigating the Effect of Linseed Oils on Lignocellulosic Paper Supports. *Analytica* **2022**, *3*, 266–286. [\[CrossRef\]](#)
18. Barclay, L.R.C.; Xi, F.; Norris, J.Q. Antioxidant Properties of Phenolic Lignin Model Compounds. *J. Wood Chem. Technol.* **1997**, *17*, 73–90. [\[CrossRef\]](#)
19. Area, M.C.; Cheradame, H. Paper aging and degradation: Recent findings and research methods. *BioRes* **2011**, *6*, 5307–5337.
20. Lazzari, M.; Chiantore, O. Drying and Oxidative Degradation of Linseed Oil. *Polym. Degrad. Stab.* **1999**, *65*, 303–313. [\[CrossRef\]](#)
21. Mills, J.; White, R. Oils and fats. In *Organic Chemistry of Museum Object*, 2nd ed.; Routledge: London, UK, 1999; pp. 31–48.
22. Gettens, R.J.; Stout, G.L. *Painting Materials: A Short Encyclopaedia*; Dover Publications: New York, NY, USA, 1966.
23. NIIR Board. Printing ink vehicles. In *The Complete Technology Book on Printing Inks*; Asia Pacific Business Press Inc.: Delhi, India, 2003; pp. 11–21.
24. Carlyle, L. MOLART Fellowship, ‘Historical Reconstructions of Artist’s Oil Paint: An Investigation of Oil Processing Methods and the Use of Medium-Modifiers’; Report no.72894 (Revised); Canadian Conservation Institute: Ottawa, ON, Canada, 2001.
25. Bonaduce, I.; Carlyle, L.; Colombini, M.P.; Duce, C.; Ferrari, C.; Ribechini, E.; Selleri, P.; Tine, M.R. New insights into the ageing of linseed oil paint binder: A qualitative and quantitative analytical study. *PLoS ONE* **2012**, *7*, e49333. [\[CrossRef\]](#)
26. Shahani, C.J. *Accelerated Ageing of Paper: Can It Really Foretell the Permanence of Paper?* *Preservation Research and Testing Series*; Report No. 9503; Library of Congress, Conservation Directorate: Washington, DC, USA, 2010.
27. Boyatzis, S. *Materials in Art and Archaeology through Their Infrared Spectra*; Nova Science Publishers, Inc.: New York, NY, USA, 2022.
28. De Viguerie, L.; Payard, P.A.; Portero, E.; Walter, P.; Cotte, M. The drying of linseed oil investigated by Fourier transform infrared spectroscopy: Historical recipes and influence of lead compounds. In *Progress in Organic Coatings*; Elsevier: Amsterdam, The Netherlands, 2016; pp. 46–60.
29. Meilunas, R.J.; Bentsen, J.G.; Steinberg, A. Analysis of aged paint binders by FTIR spectroscopy. *Stud. Conserv.* **1990**, *35*, 33–51.
30. Van der Weerd, J.; Van Loon, A.; Boon, J.J. FTIR studies of the effects of pigments on the aging of oil. *Stud. Conserv.* **2005**, *50*, 3–22. [\[CrossRef\]](#)
31. Gutiérrez, M.C. Derivative spectroscopy applied to the determination of alpha- and beta-acids in HOPS. *J. Inst. Brew.* **1992**, *98*, 277–281. [\[CrossRef\]](#)
32. Theodorakopoulos, C.; Zafiropoulos, V.; Boon, J.J.; Boyatzis, S. Spectroscopic Investigations on the Depth-Dependent Degradation Gradients of Aged Triterpenoid Varnishes. *Appl. Spectrosc.* **2007**, *61*, 1045–1051. [\[CrossRef\]](#) [\[PubMed\]](#)
33. Garside, P.; Wyeth, P. Identification of cellulosic fibres by FTIR spectroscopy. *Stud. Conserv.* **2003**, *48*, 269–275. [\[CrossRef\]](#)
34. Pavithra, R.; Gunasekaram, S.; Sailatha, E.; Kamatchi, S. Investigations on Paper Making Raw Materials and Determination of Paper Quality by FTIR-UATR and UV-Vis DRS Spectroscopy. *Int. J. Curr. Res. Aca. Rev.* **2015**, *3*, 42–59.
35. Lojewski, J.; Miskowicz, P.; Lojewski, T.; Proniewicz, L.M. Cellulose oxidative and hydrolytic degradation: In situ FTIR approach. *Polym. Degrad. Stab.* **2005**, *88*, 512–520. [\[CrossRef\]](#)
36. Young, R.A.; Rowell, R.M. (Eds.) *Cellulose: Structure, Modification, and Hydrolysis*; Wiley: Hoboken, NJ, USA, 1986.

37. Gorassini, A.; Calvini, P.; Baldin, A. Fourier Transform Infrared Spectroscopy (FTIR) analysis of historic paper: Documents as a preliminary step for chemometrical analysis. In Proceedings of the Multivariate Analysis and Chemometry Applied to Environment and Cultural Heritage (2nd Edition), CMA4CH 2008, Mediterranean Meeting, Ventone Island, Italy, 1–4 June 2008.
38. Leclerc, D.F. Fourier Transform Infrared spectroscopy in the pulp and paper industry. In *Encyclopedia of Analytical Chemistry*; Meyer, R.A., Ed.; John Wiley & Sons Ltd.: Chichester, UK, 2000; pp. 8361–8388.
39. Moutsatsou, A. Multi-parameter characterisation and dating of cellulosic substrates of modern paintings: Application to aquarelles of Greek painters. Ph.D. Thesis, National Technical University of Athens (NTUA), Zografou, Greece, 2017. Available online: <https://thesis.ekt.gr/thesisBookReader/id/39970#page/1/mode/2up> (accessed on 1 March 2023).
40. Orlova, Y.; Harmon, R.E.; Broadbelt, L.J.; Iedema, P.D. Review of the kinetics and simulations of linseed oil autoxidation. *Prog. Org. Coat.* **2021**, *151*, 106041. [\[CrossRef\]](#)
41. Ioakimoglou, E.; Boyatzis, S.; Argitis, P.; Fostiridou, A.; Papapanagiotou, K.; Yannovits, N. Thin-Film Study on the Oxidation of Linseed Oil in the Presence of Selected Copper Pigments. *Chem. Mater.* **1999**, *11*, 2013–2022. [\[CrossRef\]](#)
42. Mallégol, J.; Lemaire, J.; Gardette, J.L. Drier influence on the curing of linseed oil. *Prog. Org. Coat.* **2000**, *39*, 107–113. [\[CrossRef\]](#)
43. Izzo, F.C.; Kratter, M.; Nevin, A.; Zendri, E. A Critical Review on the Analysis of Metal Soaps in Oil Paintings. *ChemistryOpen* **2021**, *10*, 904. [\[CrossRef\]](#)
44. Hermans, J.J.; Keune, K.; Van Loon, A.; Iedema, P.D. Towards a complete molecular model for the formation of metal soaps in oil paintings. In *Metal Soaps in Art: Conservation and Research*; Casadio, F., Keune, K., Noble, P., Van Loon, E.A., Hendriks, S., Centeno, A., Osmond, G., Eds.; Springer International Publishing: Cham, Switzerland, 2019; pp. 47–67.
45. Burnstock, A. Taking Different Forms. In *Metal Soaps in Paintings, Diagnosis of Condition, and Issues for Treatment*. In *Metal Soaps in Art: Conservation and Research*; Casadio, F., Keune, K., Noble, P., Van Loon, E.A., Hendriks, S., Centeno, A., Osmond, G., Eds.; Springer International Publishing: Cham, Switzerland, 2019; pp. 243–262.
46. Artesani, A. Zinc oxide instability in drying oil paint. *Mater. Chem. Phys.* **2020**, *255*, 123640. [\[CrossRef\]](#)
47. Filopoulou, A.; Vlachou, S.; Boyatzis, S.C. Fatty Acids and Their Metal Salts: A Review of Their Infrared Spectra in Light of Their Presence in Cultural Heritage. *Molecules* **2021**, *26*, 6005. [\[CrossRef\]](#)
48. Otero, V.; Sanches, D.; Montagner, C.; Vilarigues, M.; Carlyle, L.; Lopes, J.A.; Melo, M.J. Characterisation of metal carboxylates by Raman and infrared spectroscopy in works of art. *J. Raman Spectrosc.* **2014**, *45*, 1197–1206. [\[CrossRef\]](#)
49. Gabrieli, F.; Rosi, F.; Vichi, A.; Cartechini, L.; Pensabene Buemi, L.; Kazarian, S.G.; Miliani, C. Revealing the Nature and Distribution of Metal Carboxylates in Jackson Pollock’s *Alchemy* (1947) by Micro-Attenuated Total Reflection FT-IR Spectroscopic Imaging. *Anal. Chem.* **2017**, *17*, 1283–1289. [\[CrossRef\]](#)
50. Fuster-López, L.; Izzo, F.C.; Andersen, C.K.; Murray, A.; Vila, A.; Picollo, M.; Stefani, L.; Jimenez, R.; Aguado-Guardiola, E. Picasso’s 1917 paint materials and their influence on the condition of four paintings. *SN Appl. Sci.* **2020**, *2*, 2159. [\[CrossRef\]](#)
51. Helwig, K.; Forest, É.; Turcotte, A.; Baker, W.; Binnie, N.E.; Moffatt, E.; Poulin, J. The Formation of Calcium Fatty Acid Salts in Oil Paint: Two Case Studies. In *Metal Soaps in Art: Conservation and Research*; Casadio, F., Keune, K., Noble, P., Van Loon, E.A., Hendriks, S., Centeno, A., Osmond, G., Eds.; Springer International Publishing: Cham, Switzerland, 2019; pp. 297–311.
52. Zhou, L.; Yang, X.; Xu, J.; Shi, M.; Wang, F.; Chen, C.; Xu, J. Depolymerization of cellulose to glucose by oxidation-hydrolysis. *Green Chem.* **2015**, *17*, 1519–1524. [\[CrossRef\]](#)
53. Barbash, V.; Yaschenko, O.; Alushkin, S.; Kondratyuk, A.; Posudievsky, O.; Koshechko, V. The Effect of Mechanochemical Treatment of the Cellulose on Characteristics of Nanocellulose Films. *Nanoscale Res. Lett.* **2016**, *11*, 410. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.