



Article

Oil Media on Paper: Investigating the Effect of Linseed Oils on Pure Cellulosic Paper Supports. A Research Matter of Damage Assessment

Penelope Banou ^{1,*} , Konstantinos Choulis ¹, Thanasis Karabotsos ¹, Dimitris Tsimogiannis ² , Lamprini-Areti Tsakanika ², Constantina Tzia ² and Athena Alexopoulou ¹

¹ Department of Antiquities and Works of Art, University of West Attica, Ag. Spyridonos Str., 12243 Egaleo, Greece; kchoulis@uniwa.gr (K.C.); akarab@uniwa.gr (T.K.); athfrt@uniwa.gr (A.A.)

² School of Chemical Engineering, National Technical University of Athens, Zografou Campus, 9 Iroon Polytechniou str, 15780 Zografou, Greece; ditsimog@chemeng.ntua.gr (D.T.); btsakanika@gmail.com (L.-A.T.); tzia@chemeng.ntua.gr (C.T.)

* Correspondence: pbanou@uniwa.gr; Tel.: +30-6977218522

Abstract: Oil media on paper, such as oil paintings, sketches, prints, and books, occasionally present problems associated with the effect of oil medium on the paper support, raising a composite matter of condition assessment as it depends on several factors. The present work examines the effect of linseed oil on paper and, in particular, the changes caused by three types of linseed oil on the optical, morphological, mechanical, and chemical properties of pure cellulosic paper, employing mock-ups submitted to artificial ageing in controlled conditions of relative humidity and temperature in airtight vessels. The study involved colorimetry, opacity, tensile strength, pH measurements, SEM, FTIR, and VOC analysis with GC-MS. Processing of the results has so far indicated that thermal-humid ageing caused the gradual darkening of the oil-impregnated mock-ups, as well as alterations in opacity, intense fall of pH values, and severe reductions in tensile strength, while linseed oil processing during manufacture has a significant impact. FTIR spectra have indicated that chemical changes upon ageing are in accordance with those of optical and mechanical changes, while VOC emissions are mostly associated with the drying and degradation of the different types of linseed oil.

Keywords: linseed oil; pure cellulosic paper; VOC; GC-MS; colorimetry; opacity; tensile strength; SEM; pH



Citation: 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. <https://doi.org/10.3390/analytica3010009>

Academic Editor:

Konstantinos Simeonidis

Received: 10 February 2022

Accepted: 28 February 2022

Published: 8 March 2022

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1. Introduction

Oil paintings and oil sketches on paper, prints, archival material, and books present damage, which has been associated with the effect of oil media on paper. Problems occur only when oil binders contained in oil colours and traditional oil-based printing inks are absorbed and, occasionally, diffused into the paper support [1–3]. Discolouration, decrease in pH value, loss of mechanical strength and embrittlement, and cracks and losses have been recorded on the oiled areas of the paper support with respect to works belonging to art collections worldwide [1–6]. It is worth mentioning that the problems of damage turn out irregularly and their extent varies from local and limited to overall and depend on several parameters, such as the materials and techniques used for the creation of the works.

Although the effect of the oil medium or binder on paper applies to a wide range of cultural heritage materials, only a limited number of research efforts on this matter have been published. Researchers have employed non-destructive methodology and, in particular, the Russel effect on original works of art to record the presence of free radicals on areas of linseed oil stains on paper, indicating that oxidation is taking place [4,7,8]. The oxidation of pure cellulosic papers and lignocellulosic papers has been also reported by authors based on specific volatile organic compounds (VOCs) emitted by original works

and artificially aged mock-ups and analysed with Gas Chromatography coupled with Mass Spectrometry (GC-MS) [9].

The effect of oil mediums on the mechanical properties, colour, pH, and the thermal stability of specific type of commercial paper and cardboard, with or without the applications of preparation or priming layers, after being subjected to thermal and UV light ageing for 150 h and 50 h, respectively, has been investigated by other authors [9]. They have concluded that the absorption of oil binders or the application of linseed oil as a priming layer causes the deterioration of the support when the preparation layer is missing. However, the outcome of the research did not provide information about the development of changes on the paper–oil system upon ageing [10]. Colour, pH, and mechanical changes of the paper–oil system, subjected to artificial ageing in different thermal conditions, have been studied by Banou et al. (2015), but these have not been combined with relevant chemical analysis [9]. Thus, previous results were not adequate for the interpretation of alterations and problems recorded in original works.

The investigation of the effect of oil binders on the paper supports of original works should take into consideration that the paper–oil system involves multiple parameters that influence changes upon ageing, while changes could be interrelated. Both oil and paper types present different properties due to chemical content and processing during manufacture. The selection of materials, both for oil and paper, should be representative of those used in original works, while their combination to be informative for the interpretation of the damage presented on works. In addition, artificial ageing conditions should result in changes similar to those recorded in original works at a rate that allows the determination of stages of deterioration. The effect of three types of linseed oil on the optical, morphological, mechanical, and chemical properties of pure cellulosic paper, involving mock-ups subjected to thermal-humid ageing, was investigated and the outcome will be presented in the present work. The discussion will focus more on the results of VOC analysis emitted from oil impregnated mock-ups using solid-phase microextraction (SPME) and gas chromatography coupled with mass spectroscopy. The identification of emitted compounds, the quantity, and the trend of their emission upon ageing will provide novel data on the effect of different types of linseed oil on pure cellulosic paper.

Linseed oil was chosen as the most representative oil medium used in oil painting, printing, and typography through the ages. There are references that it was used in painting in mediaeval ages, but it has been extensively applied as a binding medium for oil painting from the fifteenth century AD up to the 20th century [11–13] (pp. 42–44). It has been almost exclusively used as a binding medium for printing inks for typography and printmaking for the same period [12,14].

Pure cellulosic paper represented rag papers (flax/linen and cotton content) that were exclusively used in Europe from the 11th century up to mid-19th century AD as support for writing, printing, printmaking, and the creation of works of arts [15] (p 312). The development of industrial papermaking also introduced the use of wood pulps (wood pulp paper had started to be used regularly since the mid-19th century [15] (p 376)). Pure cellulosic papers are still used for artist quality papers and special painting and printing techniques. The methodology of research provides a holistic approach for the problems that occur due to the effect of linseed oils on pure cellulosic papers for the first time. A comparative study of the results could formulate a hypothesis on the development of damage upon ageing. This type of data has not been available before, and the condition assessment of oil media on paper could not be based on scientific evidence. The aim of the research is the identification of distinct stages of deterioration for the determination of a condition rating protocol, which is significant for decision making for the conservation and preservation of oil media collections.

2. Materials and Methods

2.1. Materials

For the mock-up's preparation, three types of linseed oil were selected that differ in the method of manufacture and consequently in physicochemical properties: Cold-pressed linseed oil (Windsor and Newton) was selected as the purest type of linseed oil used as a binder, since it has not been subjected to a thermal or chemical process; alkaline refined linseed oil (Windsor and Newton), which is the most commonly used type for oil painting, is thermally and chemically processed during manufacture (it should be mentioned that refinement procedures have been used to advance the production of linseed oil for commercial use, as well as to provide different properties. Refined linseed oils are hot-pressed and then treated to remove the bulk of undesirable impurities, known as break. The impurities present consist of suspended matter, including mucilage, albuminoid matter, resinous matter, waxes, gums, natural coloring matter, free fatty acids, and semi-volatile compounds. Historically, many refining recipes have been used, including alkali refinement that uses an alkaline solution, such as a dilute, aqueous sodium hydroxide that removes most of the break [13] (pp. 44–45 and 47)); and stand-oil (Windsor and Newton), which is pre-polymerised through long term processing in high temperature (stand-oils are more viscous than raw oil as a result of prolonged heat processing in high temperatures, with the presence or absence of air. Stand-oils today are mostly prepared by heating in the absence of air. This type of processing provides stand-oil with different properties than cold-pressed and refined linseed oil [12]).

Mock-ups were made of pure cellulosic paper. In particular, the paper used (cotton pHoton™ high purity paper by the Munktel paper Mill, Conservation by Design Limited, UK) is made of 100% pure cotton linters, and it is unbuffered, with no fillers or sizing, 80 gsm. Fibre analysis using optical microscopy, EDX analysis, and FTIR analysis were performed to provide information about fibre and pulp content. This paper type provides the purest form of paper.

2.2. Preparation of Mock-Ups and Artificial Ageing

Paper strips, 2.5 × 20 cm (width × length), were cut for the preparation of four sets of mock-ups: one set of plain paper mock-ups and three sets to be fully impregnated with 0.6 mL of the three types of linseed oil, respectively, using a syringe. Extra four sets of mock-ups were prepared only for VOC analysis, possessing half the size of the length, 2.5 × 10 cm (width × length), impregnated with 0.3 mL of linseed oils, correspondingly, so that they could be fitted (folded in half) in headspace vials by the end of every stage of artificial ageing. These were weighed before and after oil application at 23 °C and 55% RH.

The size of the mock-ups was selected to serve the criteria or standards of the methods of investigation or analysis applied, while the volume of oil was adequate for uniformly impregnating the paper strips, without leaving excess.

After 40 days of air drying in dark conditions, the mock-ups were subjected to artificial ageing in controlled conditions of 77% relative humidity (engaging saturated solution of sodium chloride, 15% *w/v*) and temperature of 80 °C in airtight vessels for 2, 4, 7, 14, 21, and 28 days. 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].

2.3. Methods

The research involved colorimetry, opacity, tensile strength, and pH measurements adopting the methodology recommended by TAPPI test methods, as well as SEM, FTIR, and VOC analysis with GC-MS.

2.3.1. Colour

Colour changes have been investigated with CIELab* colour system and reflectance measurements following standard TAPPI T 527 om-02 [19] by using a colorimeter with

an integrating sphere (PCE-CSM 10) over a white surface (reflectance more than 89%). The changes were expressed as ΔE^* , taking into consideration the differences in L^* , a^* , and b^* coordinates. L^* , a^* , and b^* are used to designate colour values as follows: L^* represents lightness increasing from zero for black to 100 for perfect white; a^* represents redness when positive and greenness when negative; and b^* represents yellowness when positive, blueness when negative. Colour difference ΔE^* was calculated by the following formula [19].

$$\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$$

For every stage of ageing, ΔE^* corresponds to the average value of measurements on three mock-ups, resulting from the average of measurements on three different points of each mock-up. For each point, the average of three measurements is considered. Thus, each ΔE^* is the mean value of nine measurements.

All sets of mock-ups were recorded with visible light photography, using a digital camera Nikon D70s with AF micro NIKKOR 60 mm lens, with flashlights, in conditions of a shutter speed of 125 and f-number of 11.

2.3.2. Opacity

The opacity of the mock-ups was evaluated by the contrast ratio of the reflectance recorded over a black backing divided by the reflectance over a white backing and type 89% backing, according to TAPPI test method T 425 om-16 [20], using a colorimeter with an integrating sphere (PCE-CSM 10). In particular, we have the following.

$$\text{Opacity (\%)} = \frac{Y_{black}}{Y_{white}} \times 100$$

For every stage of ageing, the opacity value is the result of the average of measurements on three mock-ups for every stage of ageing, which resulted in the average of measurements on three different points on each mock-up on white and black backings.

2.3.3. Morphological Changes

To study the morphological changes on the surface of the paper–oil system, mock-ups were examined with a Scanning Electron Microscope (JEOL JSM-6510LV), with variable pressure, equipped with backscattered electrons (BSE) and detector. SEM was operated at 20 keV and a high resolution of 3 nm using a secondary electron signal (SEI). The specimens were observed in conditions of high vacuum, 10^{-9} Torr. Mock-ups were coated with gold–cobalt alloy to enhance conductivity, placed on a sulphur-free carbon adhesive (Spectrotabs AGG3358, Agar Scientific), and adhered onto an aluminium stub (1.25 cm diameter, Agar Scientific).

SEM was coupled with an energy dispersive X-ray spectrometer (EDX: model X-Act, Oxford Instruments Inc) incorporating INCA software. EDX analysis was employed for the elemental analysis of paper used for the preparation of samples.

2.3.4. Mechanical Changes

Mechanical changes were studied with tensile strength measurements. These were taken according to the TAPPI test method T494 [21] using the testing system Instron 3400 series. The number of measurements for every ageing stage was 10 for all sets of mock-ups, five for each principal direction of the paper (parallel and cross-grain direction). Measurements were taken in room conditions of 23 °C and 50% RH, and the conditions of the mock-ups were the same conditions for 24 h.

2.3.5. Chemical Changes

pH measurements, FTIR, and analysis of volatile organic compounds (VOC) emitted by the mock-ups upon ageing using Gas Chromatography coupled with Mass Spectroscopy (GC-MS) were applied for the study of chemical changes of the paper–oil system.

pH Changes

pH values of mock-ups were obtained by cold extraction pH measurements according to the TAPPI test method T509 om-02 [22], with a pH measuring unit (SCHOTT Instruments, pH meter LAB 850). The values resulted from the average of measurements on three mock-ups for every stage of ageing for all sets of mock-ups. Measurements were taken in room conditions of 23 °C and 50% RH.

FTIR Analysis

Fourier Transform Infrared (FTIR) analysis was performed to investigate the chemical changes of the paper–oil system upon ageing, using a Jasco 4200 spectrometer with TGS detector supplied by Jasco Corporation (Tokyo, Japan). A range of 4000–400 cm^{-1} with a resolution of 4.0 cm^{-1} and 32 scans were selected. All samples were pelletised using KBr of FTIR grade (221864, Honeywell, Charlotte, NC, USA) on powdered samples. IR spectra were performed in transmission mode. Spectra delivered after the extraction of water (H_2O) and carbon dioxide (CO_2) have been processed with baseline correction.

Analysis of Volatile Organic Compounds with SPME-GC-MS

VOCs were sampled by inserting the SPME needle in the head-space of septum tight-sealed vials that contained a mock-up. The coated tip of the fibre was placed at a very close distance from the mock-ups. For the extraction of VOCs, the SPME needle cartridge with a 50/30 m divinylbenzenecarboxen/poly(dimethylsiloxane) fibre (Supelco, Sigma-Aldrich Ltd., Dorset, UK) was preconditioned by heating to 230 °C in the injection port of a GC-MS and retracted. The preconditioned SPME needle was then inserted into a headspace vial (Screw neck vials N24, 40 mL with lid PP, white, centre hole, silicon white/PTFE beige septum, hardness 45°, shore A, thickness 3.2 mm, LLG-Labware), containing the impregnated paper sample, for 30 min at 25 °C (room temperature). The SPME needle was then retracted and reopened in the injection port of the GC-MS and heated to 230 °C for 10 min to release volatile components to the column. The compounds were then separated and identified by GC-MS analyses carried out in an Agilent Technologies 7890A GC gas chromatograph coupled to an Agilent Technologies 5975 C MSD mass selective detector and an Agilent 1909/S capillary column (30 m \times 0.25 mm internal diameter; coating thickness 0.25 mm). The carrier gas used was He, with a flow rate of 1 mL/min at splitless mode. The temperature of the column started at 43 °C and raised without hold time from 43 °C to 60 °C at a rate of 2.5 °C/min and then to 230 °C at a rate of 15 °C/min. The temperature was then maintained constant for 12 min. Subsequently, oven temperature was raised to 240 °C for a post-run period of 5 min for column clean-up. The identification of compounds was performed according to the comparison of the MS spectrum of each peak with the internal database. The peak areas were quantified according to selected ions, producing non-overlapping peaks with nearby eluting compounds, while for each identified compound, three additional ions were used as qualifiers for the detection of each component.

3. Results and Discussion

3.1. Colour Changes

Thermal-humid conditions of ageing resulted in a gradual darkening of oil-impregnated mock-ups, with distinct variations between the stages of ageing (Figure 1), while plain cotton mock-ups (C) did not present any notable changes, which is confirmed by the fact that the ΔE^* difference is less than 2 for all ageing stages (the minimal detectable difference is between 1 and 2 Delta E [23,24]). However, mock-ups impregnated with stand-oil (C+StL) presented more limited changes, a fact attributed to oil processing during manufacture [12], p. 41. On the other hand, mock-ups impregnated with refined linseed oil (C+Rf) appear to be darker than the mock-ups of the other two sets at all stages, respectively.

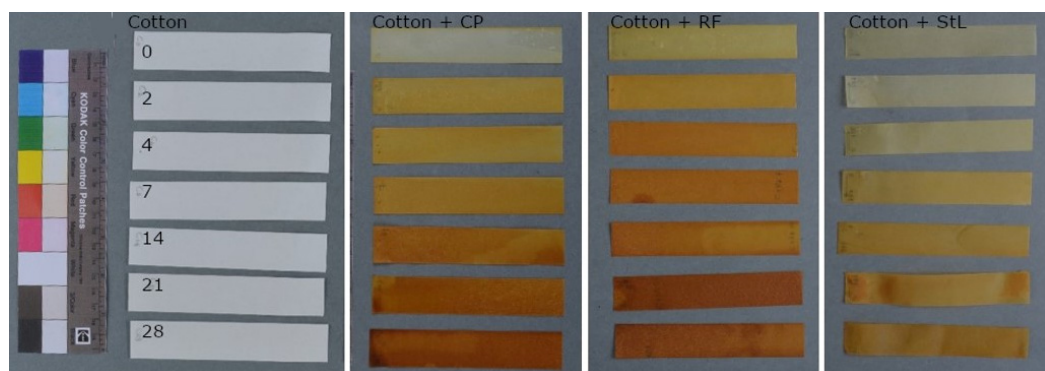


Figure 1. The four sets of mock-ups recorded with visible light photography.

These observations were confirmed by the reflectance spectra (Figure 2) and colour difference ΔE^* values derived from all sets of mock-ups at all ageing stages (Figure 3). However, the trend of changes is quite similar with few variations. The differences are located in the first stages of ageing (up to the 7th day of ageing), while the trend is comparable after the 14th day of ageing (Figures 2 and 3). In particular, the colour change between the second and fourth days of ageing is similar for C+CP and C+StL mock-ups in comparison to that of the C+RF mock-ups which is more intense. This is reversed between the fourth and seventh day, where the colour difference is more intense for C+CP and C+StL in comparison to that of C+RF mock-ups. The colour difference after the 14th day of ageing is mild and becomes almost flattened after the 21st day of ageing.

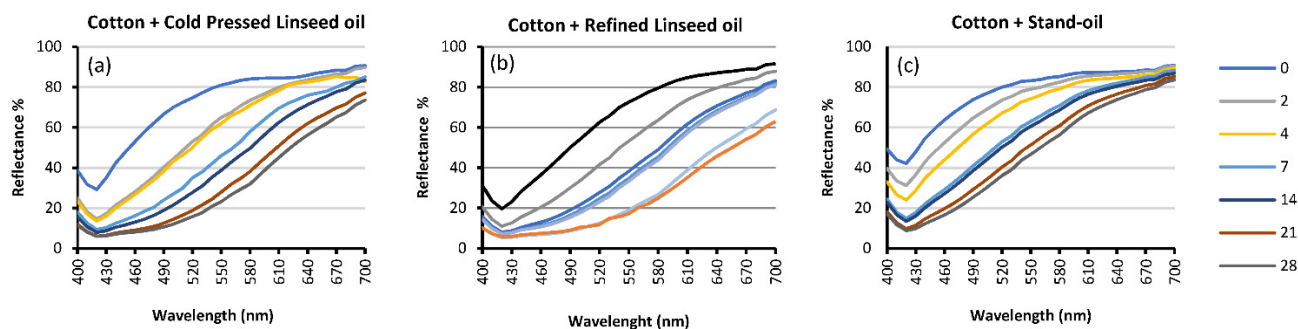


Figure 2. Reflectance graphs of all sets of mock-ups, including measurements of 0, 2, 4, 7, 14, 21, and 28 days: (a) set of cotton mock-ups impregnated with cold-pressed oil; (b) set of cotton mock-ups impregnated with refined linseed oil; (c) set of cotton mock-ups impregnated with stand-oil.

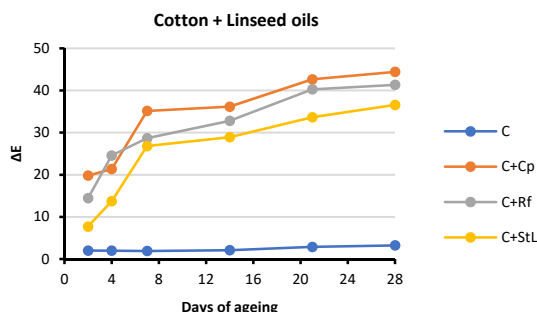


Figure 3. Graph representing colour changes (ΔE^*) of all sets of mock-ups upon ageing.

3.2. Opacity Changes

The results have shown that the application of all types of linseed oil caused a reduction in the opacity of mock-ups, which is evident by comparison with plain mock-ups in the graph shown in Figure 4. Upon ageing, the opacity of oil-impregnated mock-ups tended to increase at a mild pace, with those impregnated with cold-pressed (C+CP) and refined

linseed (C+RF) oil presenting a common trend. However, the opacity of the mock-ups impregnated with refined linseed oil is higher at 28 days of ageing. On the other hand, the opacity changes of mock-ups impregnated with stand-oil (C+StL) are limited and remain almost stable after the 14th day. It could be suggested that the high density and possibly the pre-polymerisation of stand-oil during manufacture differentiated the behaviour of mock-ups upon ageing.

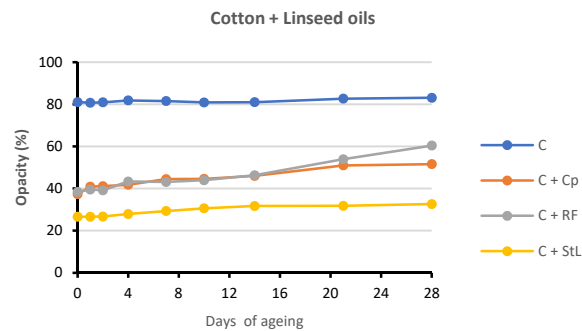


Figure 4. Graph representing the opacity changes of all sets of mock-ups.

3.3. Morphological Changes

SEM images showed that the loose fibre net of cotton paper (Figure 5) was covered with a gelatinous film 40 days after linseed oil application on mock-ups, which followed the relief of the surface (Figures 6 and 7). Images indicated that linseed oil upon drying formed a “gel” that filled and constrained the fibre net. Upon ageing, the oil film appeared to recess, holes gradually opened locally, and, by the final stages, the fibres became exposed. This is in accordance with oil degradation upon ageing, in which oil shrinks and becomes brittle [25]. Oil impregnated mock-ups with cold-pressed and refined linseed oil provided similar images. On the other hand, images indicated that the recession of highly viscous stand-oil was milder and possibly occurred at a slower pace (Figure 7).

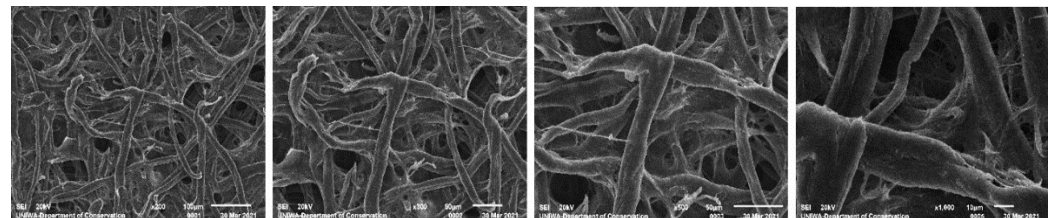


Figure 5. SEM images of cotton paper, 0 days of ageing, at 200 \times , 300 \times , 500 \times , and 1000 \times magnification (left to right).

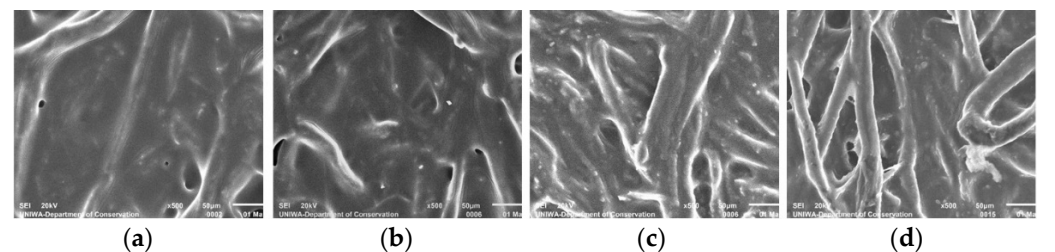


Figure 6. SEM images of cotton mock-ups impregnated with cold-pressed linseed oil at different stages of ageing, at 500 \times magnification: (a) 0 days of ageing, after 40 days of air-drying; (b) 4 days of ageing; (c) 14 days of ageing; (d) 21 days of ageing.

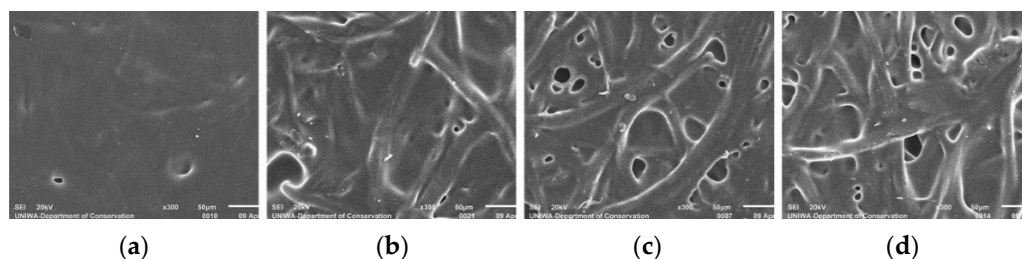


Figure 7. SEM images of cotton mock-ups impregnated with stand-oil at different stages of ageing, at 500× magnification: (a) 0 days of ageing, after 40 days of air-drying; (b) 7 days of ageing; (c) 14 days of ageing; (d) 21 days of ageing.

3.4. Mechanical Changes

Thermal-humid ageing did not cause any notable changes to the tensile strength of plain paper mock-ups (C), while the impregnated mock-ups with all types of linseed oil presented a common trend of change with limited variations (Figure 8). The application of linseed oils on cotton paper caused a significant increase in tensile strength after 40 days of ageing (average 22%). The tensile strength of the mock-ups gradually decreased up to the fourth day of ageing, obtaining measurements close to those of the plain ones, while at the following stages, the fall was more intense. After 28 days of ageing, the tensile strength of the impregnated cotton mock-ups decreased up to 80% (Figure 8).

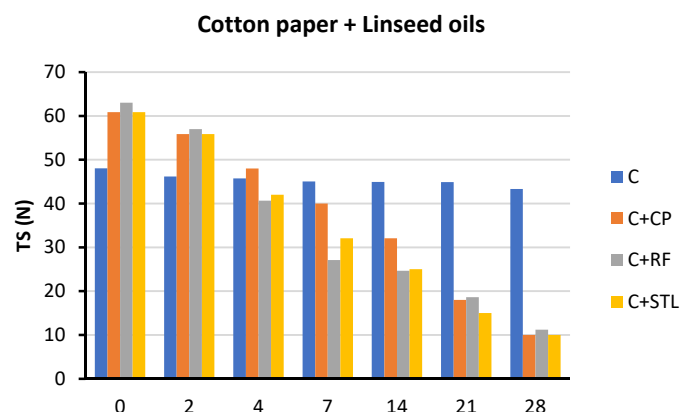


Figure 8. Graph showing the changes of tensile strength of all sets of mock-ups at all ageing stages.

3.5. Chemical Changes

3.5.1. pH Measurements

pH measurements showed that the application of linseed oil of all types causes a decrease in pH value by an average of 2 points, after 40 days of air drying. However, upon ageing, the decrease in pH values of all mock-ups upon ageing is limited and variable (Table 1).

Table 1. pH measurements.

| Days of Ageing | C | C + Cp | C + Rf | C + StL |
|----------------|-----|--------|--------|---------|
| 0 | 6.8 | 4.7 | 5.0 | 4.7 |
| 1 | 6.7 | 4.4 | 4.8 | 4.5 |
| 2 | 6.4 | 4.7 | 5.4 | 4.2 |
| 4 | 6.4 | 4.7 | 4.5 | 4.2 |
| 7 | 6.3 | 4.2 | 4.5 | 4.2 |
| 10 | 6.1 | 4.0 | 4.5 | 4.2 |
| 14 | 6.2 | 4.6 | 4.3 | 4.4 |
| 21 | 6 | 4.8 | 4.5 | 4.2 |
| 28 | 6.4 | 4.3 | 4.8 | 3.9 |

3.5.2. FTIR Analysis

FTIR analysis has been reported in numerous research works on different types of paper and linseed oil, yet the reports focus on each component individually and not as a system [11,26–33]. Paper degradation occurs through oxidation and acid hydrolysis processes. The oxidation of cellulose results in the formation of carbonyl-containing groups (aldehydes and ketones) and carboxylic groups (carboxylic acids). Hydrolysis is induced in the presence of water, in acidic conditions, and results in breaking the cellulose chain into smaller parts. Hydrolysis and oxidation processes are dependent on each other and catalyse each other as oxidation contributes to the creation of carboxyl groups, thus promoting acid hydrolysis [34].

Linseed oils belong to the category of drying oils that harden or “dry” into a solid film when exposed to daylight and ambient oxygen. The drying of linseed oil is considered as polymerization of triglycerides via autoxidation, a process involving free radicals, followed by cross-linking polymerization. Polymerization competes with degradation processes such as scission reactions, decomposition of unstable crosslinks, and hydrolysis [35,36].

In the current work, FTIR analysis confirmed the use of pure cellulosic (cotton-based) paper according to the results of previous works [26,28]. The band at 999 cm^{-1} has been regarded as the fingerprint of cellulose in papers, as well as the C-C ring breathing band at $\sim 1105\text{ cm}^{-1}$ and the C-O-C glycosidic ether at $\sim 1155\text{ cm}^{-1}$. Other characteristic bands related to the chemical structure of cellulose are hydrogen-bonded OH stretching at around $3550\text{--}3100\text{ cm}^{-1}$, CH stretching at 2917 cm^{-1} , and CH wagging at 1316 cm^{-1} .

FTIR spectrum of fresh-uncured linseed oil includes 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. In addition, 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 1652 cm^{-1} , the CH deformations at $1000\text{--}800\text{ cm}^{-1}$, and the C-C stretching vibrations at $1680\text{--}1600\text{ cm}^{-1}$ [11,32].

As it is shown in Figure 9a, FTIR spectra of plain cotton mock-ups did not display notable changes upon ageing, while oil-impregnated mock-ups have so far displayed moderate changes in specific bands of the spectrum upon ageing (Figure 9b–d). Stronger bands were observed due to the gradual reduction in transmittance %T (increase in absorption) in the bands that respond to carbonyl-containing species (such as aldehydes and ketones) and carboxyl acids ($1600\text{--}1750\text{ cm}^{-1}$), which are associated both with cellulose oxidation as well as the oxidation of linseed oil [27,29,30]. A transmittance reduction (increase in absorption) has also been noted for 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, which 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 [30].

Variations in bands are possibly associated with the process of linseed oil manufacture (Figure 9b–d). More significant changes are recorded for the mock-ups subjected to artificial ageing for 14 days and more. Still, oil-impregnated mock-ups with stand-oil present limited changes on the bands attributed to polymerization. However, changes in paper chemistry could not so far be determined due to overlapping peaks with the bands of interest referring to linseed oil degradation. Further study is required for the study of the changes in specific bands and the correlation with the results of the other methods of study.

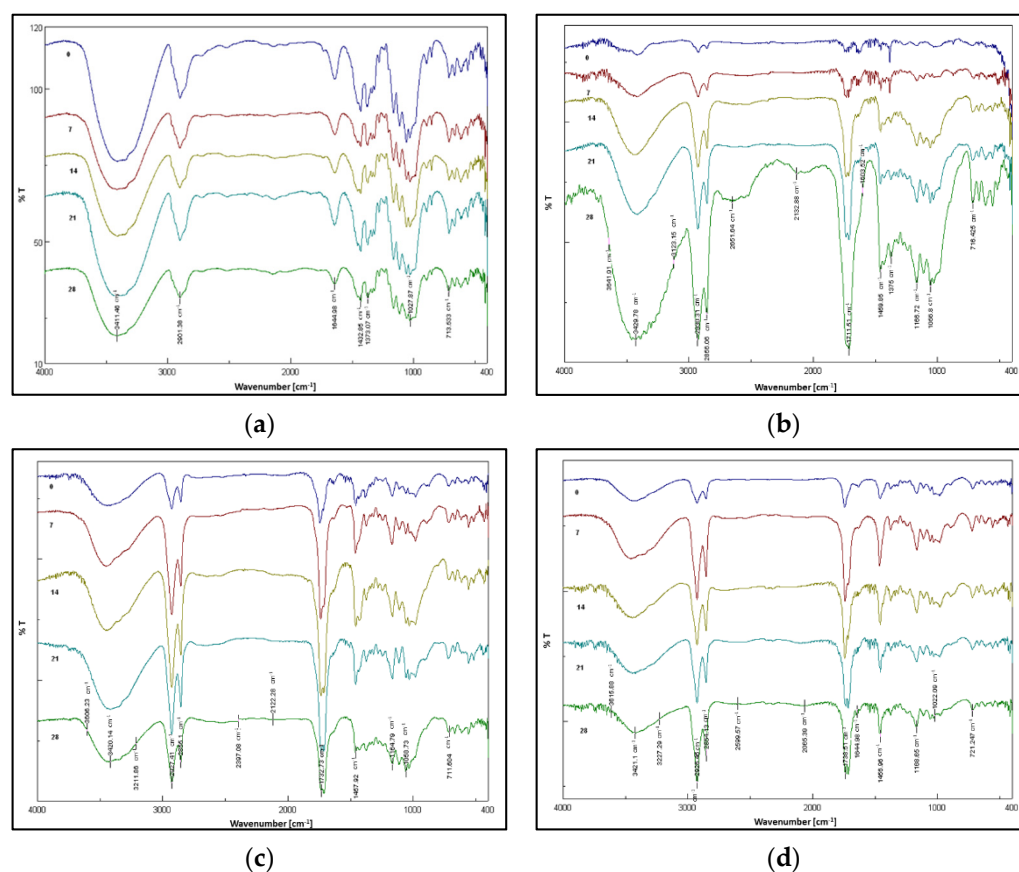


Figure 9. FTIR spectra of the four sets of mock-ups at various ageing stages: (a) plain cotton mock-ups; (b) cotton mock-ups impregnated with cold-pressed linseed oil; (c) cotton mock-ups impregnated with refined linseed oil; (d) cotton mock-ups impregnated with stand-oil.

3.5.3. Analysis SPME-GC-MS

VOCs were sampled non-destructively by means of extraction without the application of a solution or incubation in elevated temperatures to promote the emission of compounds used in previous studies [8,17,18,37]. Non-destructive application has been successfully used before by placing the needle at the surface of samples or mock-ups or between two sheets of books in an open space or restricted in inert packages [38–41]. In addition, VOC sampling/extraction with an SPME needle from oil sketches and prints encased in a glass structure to constrain environmental contamination has been used in previous work [8]. Wetting with a solution or incubation does not apply to original works. In addition, a non-destructive methodology of application was selected for the mock-ups in the present study, taking into consideration that the results on mock-ups would be used as references determining the stages of ageing or deterioration on original works. Trials of VOCs extraction employing HS-SPME and contact sampling, while the mock-ups remained in the vials without the lid, did not present significant variations.

Solid Phase Microextraction (SPME) has been used for VOC extraction both from paper and linseed oil, while DVBCAR/PDMS (divinylbenzene-carboxen/poly(dimethylsiloxane)) coating has been regarded to be the most effective in relevant research works [17,42].

In this current work, GC-MS analysis of all sets of oil-impregnated mock-ups has identified 30 volatile organic compounds that belong to several chemical classes: saturated and unsaturated aldehydes, ketones, alcohols, carboxylic acids, lactones, and furans (Table 2). Aldehydes compounds comprise hexanal, 2-hexenal, heptenal, 2-heptanal, octanal, 2-octenal, nonanal, 2-nonenal, decanal, 2-decenal, and 2-undecanal. Ketones include 2-heptanone, 2-octanone, 4-nonanone, 2-nonanone, and 2-decanone. Lactones include gamma heptalactone and gamma-nonalactone, while alcohols only include 1-octen-3-ol.

Table 2. Compounds emitted by all sets of mock-ups.

| No. | Compounds | r.t. (min) | Quantification Ion (m/z) | Identification Ions (m/z) |
|-----|--------------------------|---------------|-----------------------------|------------------------------|
| 1 | methanoic acid (formic) | 1.47 | 46 | 44, 45, 43 |
| 2 | ethanoic acid (acetic) | 1.78 | 60 | 43, 45, 42 |
| 3 | propanoic acid | 3.61 | 74 | 73, 57, 45 |
| 4 | Hexanal | 4.03 | 56 | 44, 72, 82 |
| 5 | 2-hexenal | 5.36 | 55 | 69, 83, 98 |
| 6 | 2-heptanone | 6.52 | 43 | 58, 71, 114 |
| 7 | Heptanal | 6.88 | 70 | 55, 81, 96 |
| 8 | pentanoic acid | 7.56 | 60 | 73, 41, 55 |
| 9 | 2-heptenal | 8.40 | 83 | 55, 70, 112 |
| 10 | 1-octen-3-ol | 8.92 | 57 | 72, 85, 99 |
| 11 | 2-pentyl-furan | 9.04 | 81 | 53, 95, 138 |
| 12 | 2-octanone | 9.14 | 58 | 71, 128, 113 |
| 13 | Octanal | 9.38 | 84 | 69, 100, 57 |
| 14 | 5-ethyl-2-(5H)-furanone | 9.98 | 83 | 55, 112 |
| 15 | hexanoic acid | 10.10 | 60 | 73, 87, 41 |
| 16 | 2-octenal | 10.30 | 83 | 55, 70, 108 |
| 17 | 4-nonanone | 10.51 | 43 | 71, 99, 142 |
| 18 | 2-nonanone | 10.80 | 58 | 71, 142 |
| 19 | Nonanal | 10.97 | 57 | 41, 70, 98 |
| 20 | heptanoic acid | 10.89 | 60 | 73, 87, 101 |
| 21 | gamma heptalactone | 11.62 | 85 | 56, 71, 110 |
| 22 | 2-nonenal | 11.68 | 41 | 70, 83, 96 |
| 23 | octanoic acid | 12.02 | 60 | 73, 101, 115 |
| 24 | 2-decanone | 12.06 | 58 | 43, 71, 156 |
| 25 | Decanal | 12.21 | 57 | 82, 112, 128 |
| 26 | 2-decenal | 12.82 | 41 | 70, 83, 98 |
| 27 | nonanoic acid | 12.97 | 60 | 73, 115, 129 |
| 28 | 5-pentyl-2-(5H)-furanone | 13.67 | 84 | 55, 125, 154 |
| 29 | 2-undecanal | 13.82 | 70 | 57, 83, 124 |
| 30 | gamma-nonalactone | 13.86 | 85 | 114, 128, 100 |

Listed in order of increasing retention time. The compounds correspond to internal standards.

Carboxylic acids encompass methanoic (formic), ethanoic (acetic), propanoic, pentanoic, hexanoic, heptanoic, octanoic, and nonanoic acids. Finally, furans include 2-pentyl furan, 5-ethyl-2(5H)-furanone and 5-pentyl-2-(5H)-furanone.

These compounds have been associated with the oxidation of linseed oil and papers [17,18,39–45]. The majority of VOCs detected have been reported in studies on linseed oil with different origins, extraction methods and processes during manufacture (virgin/raw and refined) for different uses (food, cosmetics, and painting materials), with or without being accelerated storage or oxidation conditions [42–47]. On the other hand, hexanal, heptanal, octanal, nonanal, and decanal have been detected in historical books with pure cellulosic fibre content (Flax/linen) [39], but they were regarded irrespective of paper composition. They have been attributed to the lipid content of books.

To study the evolution of the emission of VOCs, the results were included in sum up graphs for every chemical group: acid, aldehydes, ketones, and furans. For all three sets of oil-impregnated mock-ups, the emission of acids was comparatively higher than the other chemical groups and presented a common trend: a gradual decrease up to the 28th day of ageing (Figure 10a, Figure 11a, and Figure 12a). However, their emissions remained at a high level in comparison with other chemical groups. Among the three sets, mock-ups impregnated with stand-oil present a lower emission of acids and a comparatively limited decrease (Figure 12a). Formic, propanoic, hexanoic, and acetic acids presented higher emissions than the rest for all sets of mock-ups.

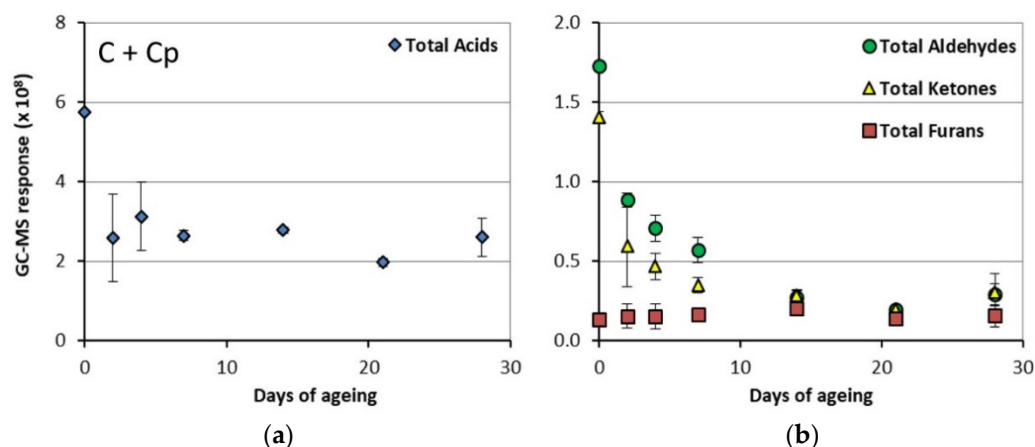


Figure 10. The evolution of the basic chemical groups of VOCs' emission by cotton mock-ups impregnated with cold-pressed linseed oil upon ageing: (a) acids; (b) aldehydes, ketones, and furans.

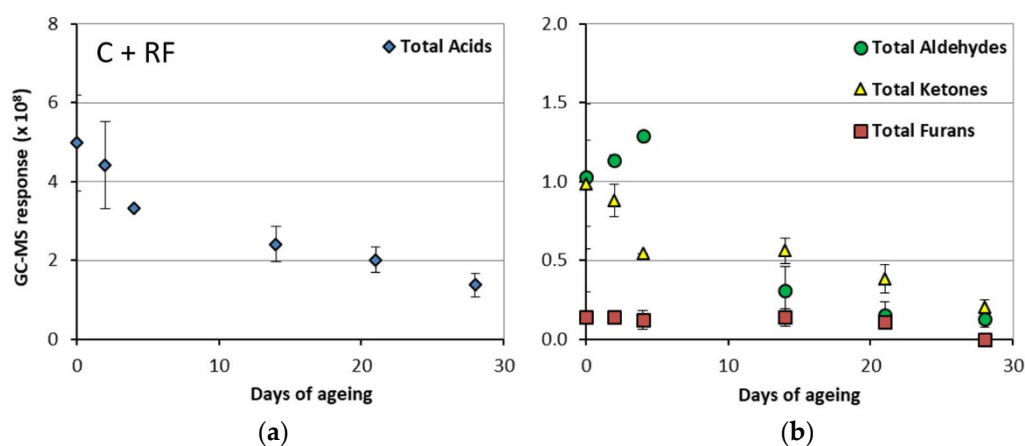


Figure 11. The evolution of the basic chemical groups of VOCs' emission by cotton mock-ups impregnated with refined linseed oil upon ageing: (a) acids; (b) aldehydes, ketones, and furans.

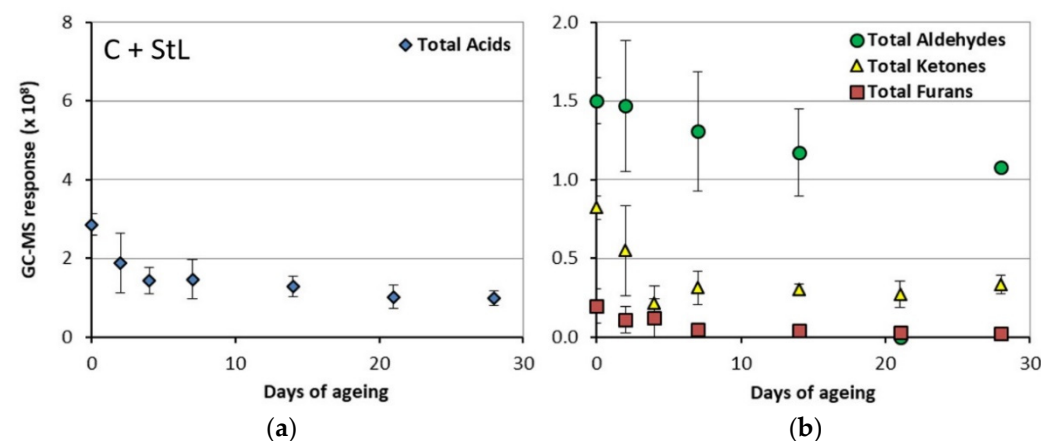


Figure 12. The evolution of the basic chemical groups of VOCs' emission by cotton mock-ups impregnated with refined linseed oil upon ageing: (a) acids; (b) aldehydes, ketones, and furans.

Emissions of aldehydes were much lower than those of acids (their higher emissions responded to the lower emissions of acids), and their trend differed in the three sets of mock-ups (Figures 10–12). For the mock-ups impregnated with cold-pressed linseed oil, the emissions gradually decreased upon ageing (Figure 10b). For the mock-ups impregnated with refined linseed oil, the emission presented an increase up to the fourth day of ageing

and then a gradual decrease up to the 28th day of ageing (Figure 11b). For the mock-ups impregnated with stand-oil, the emission was relatively stable upon ageing (Figure 11b). Emissions of ketones were lower than those of aldehydes for all sets of mock-ups. They presented a common trend of a gradual decrease in a similar quantity, up to the 28th day of ageing (Figure 10b, Figure 11b, and Figure 12b).

For all three sets of oil-impregnated mock-ups, the emission of furans was comparatively lower than the other chemical groups and appeared almost stable with a limited falling tendency up to the 28th day of ageing (Figures 10b, 11b and 12b). Again, the emissions of the mock-ups impregnated with stand-oil were very low (Figure 12b). Finally, the emissions of lactones and alcohol were significantly low and presented a similar trend for all sets of mock-ups.

The emissions of the chemical groups, especially those of acids, aldehydes, and ketones and their trends, respectively, could be associated with the kinetics involved with the drying and degradation of linseed oils [42,46,47]. It could be suggested that extensive oxidation of linseed oil and the consequent polymerisation inhibit the emission of volatile organic compounds upon drying. The formation of the polymer matrix could act as a barrier for VOCs emission. This could provide a hypothesis for the decrease in VOCs emission upon ageing.

It is evident that the linseed oil process of manufacture influences the quantity and trend of emission. Processing stand oil results in a much slower drying, with the uptake of much less oxygen [12], p. 41. This could provide a possible explanation for the stable trend of aldehydes and the lower emission of acids. It could also be suggested that the alkaline process also has an effect on the emission of aldehydes.

Further work is required for the evaluation of the results. The processing of emission results of every compound is regarded as necessary to export data useful for the condition assessment of oil-impregnated paper areas on original works of art.

4. Conclusions

The comparative study of the results indicated that linseed oils have a major impact on changes recorded in several sets of mock-ups. Although all three sets of oil-impregnated mock-ups present common trends in the changes of optical properties (colour and opacity), morphological properties, and mechanical properties, the variations recorded could be associated with the differences in processing during oil manufacture and the resultant effect on drying rates and the oxygen uptake.

Drying rates of the three linseed oils could have possibly influenced the trend of colour differences upon ageing between the sets of mock-ups. Likewise, the drying rate and high viscosity of stand-oil resulted in milder recessing of the oil into the fibre net and more limited morphological changes.

Opacity, which is associated with the refractive index of the paper–linseed oil system, could be influenced both by colour and morphological changes. Limited colour changes of stand-oil and slower recess into the fibre net could explain the limited changes in the opacity of the mock-ups.

The changes presented in the FTIR spectra appear to be in accordance with the changes recorded for the sets of mock-ups with other methods of study. Although there are differences in the changes of the several bands of the spectra between the mock-ups impregnated with cold-pressed and refined linseed oil with those impregnated with stand-oil, the development of linseed oil degradation in conditions of thermal-humid ageing possibly creates acidic conditions that induce the acid hydrolysis of cellulose. This could explain the severe collapse of tensile strength of all sets of mock-ups after the 14th day of ageing in conditions of thermal-humid ageing. Moreover, FTIR spectra present more intense changes after the 14th day of ageing for all sets of mock-ups.

Finally, VOC's emission appears to be influenced by linseed oil processing. However, emissions gradually decreased and remained comparatively low after the 14th day of ageing.

The methodology of artificial ageing has succeeded to reproduce the changes in optical, mechanical, and chemical properties, similarly to those recorded in original works. The rate of ageing and the resulting changes could provide indications for the determination of stages of deterioration. The selected methodology of research is informative for the development of changes; thus, it could be used as a basis for further investigations of the effect of oil binders on paper support in the future.

Although the aforementioned results require advanced processing in order to establish certain stages of deterioration, the input of the results is significant on the research matter with respect to the effect of linseed oils on pure cellulosic papers in a holistic approach. The use of a certain type of linseed oil is decisive for the development of changes upon ageing. The outcome of this work will compensate the condition assessment of works created with oil media on paper, which is associated with conservation and preservation decision making for a wide range of cultural heritage objects.

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

Funding: This work was performed in the framework of a PhD research project, and it has not received any funds from external sources.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

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

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