

Oxidation and Cross-Linking in the Curing of Air-Drying Artists' Oil Paints

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Cite This: *ACS Appl. Polym. Mater.* 2021, 3, 1912–1922

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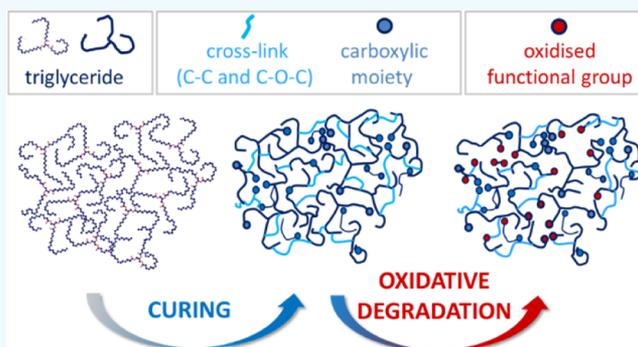
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ABSTRACT: In this study, the chemistry of air-drying artist's oil paint curing and aging up to 24 months was studied. The objective is to improve our molecular understanding of the processes that lead to the conversion of the fluid binder into a dry film and how this evolves with time, which is at the base of a better comprehension of degradation phenomena of oil paintings and relevant to the artists' paint manufacturing industry. To this aim, a methodological approach based on thermogravimetric (TG) analysis, differential scanning calorimetry (DSC), gas chromatography–mass spectrometry (GC–MS), and analytical pyrolysis coupled with gas chromatography and mass spectrometry (Py–GC–MS) was implemented. Model paintings based on linseed oil and safflower oil (a drying and a semidrying oil, respectively) mixed with two historically relevant pigments—lead white (a through drier) and synthetic ultramarine blue (a pigment often encountered in degraded painting layers)—were investigated. The oil curing under accelerated conditions (80 °C under air flow) was followed by isothermal TG analysis. The oxygen uptake profiles were fit by a semiempirical equation that allowed to study the kinetics of the oil oxidation and estimate oxidative degradation. The DSC signal due to hydroperoxide decomposition and radical recombination was used to monitor the radical activity over time and to evaluate the stability of peroxides formed in the paint layers. GC–MS was performed at 7 and 24 months of natural aging to investigate the noncovalently cross-linked fractions and Py–GC–MS to characterize the whole organic fraction of the model paintings, including the cross-linked network. We show that the oil–pigment combination may have a strong influence on the relative degree of oxidation of the films formed with respect to its degree of cross-linking, which may be correlated with the literature on the stability of painting layers. Undocumented pathways of oxidation are also highlighted.

KEYWORDS: air-drying artists' oil paints, linseed oil, safflower oil, lead white, ultramarine blue, lipid autoxidation, oil curing



1. INTRODUCTION

Paint consists of finely divided pigment particles—the discontinuous phase—dispersed in an organic fluid binder—the continuous phase. When a drying oil, which is a plant oil made of triglycerides of polyunsaturated fatty acids, is used as the binder, the paint is an oil paint.¹ Despite the introduction of synthetic paints, oil paints are still vastly used by artists due to their working properties and to the optical quality of the paint films they produce.² Plant oils are also employed to produce high-solid and water-borne (WB) formulations used in protective and decorative coatings.^{1,3–5}

Oil binders cure by the action of oxygen, and films are formed through chemical reactions that solidify and harden the oil. The curing of an oil paint is an autoxidative process^{6,7} involving the formation of peroxide species, which evolve the following two main competitive phenomena—cross-linking and oxidation.^{1,8–11} Cross-linking is fundamental for obtaining a durable film that keeps the pigment particles together and adherent to the support.

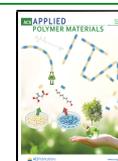
Much research has investigated lipid oxidation^{8,9} in the context of food,^{6,7,12–16} lipid biochemistry,^{17,18} and air-drying paints intended for industrial applications and the do-it-yourself market.^{1,19–21} The complexity of reactions taking place over time in air-drying artistic oil paint layers is still the focus of research, especially in relation to degradation phenomena in paintings.^{8,10,22–30}

Although pigments undergo chemical modifications that have an impact visually on the painting, the weakest link in the paint durability is the film former:¹ chemical changes in the continuous phase are reflected in changes in the mechanical properties of the paint layer, thus affecting its stability, and its

Received: December 31, 2020

Accepted: March 4, 2021

Published: March 16, 2021



response to the external environment and conservation interventions.

In heritage science, it is well known that the degradation of the organic film in an oil paint is strongly dependent on both internal and external factors such as the oil type,^{11,31–33} the pigment(s),^{10,28–30,32–37} additive(s),^{1,21,28} artistic practices,^{11,23,29,30} environmental conditions,^{26,29,30,38} and conservation practices.^{39,40} The chemical nature of the changes occurring in the film former as a consequence of degradation is, in most cases, not fully understood at the molecular level. It was recently hypothesized that some degradation phenomena taking place in oil paintings—especially those produced with modern manufactured artists' oil paints²—are related to the chemical nature of the oil cross-linked network and, in particular, to a low degree of polymerization and a high degree of oxidation.^{10,23,25,31,41}

Unfortunately, the molecular characterization of the polymeric network formed in a paint film is still a big challenge from an analytical point of view.¹⁰ However, a useful approach to improve our understanding of the chemical structure of an oil polymeric film is to characterize the process leading to its formation: the curing.

In this work, the chemistry of oil curing and aging up to 24 months was studied in model paintings. Linseed and safflower oils were selected as drying and semidrying oils, respectively. Of the drying oils, linseed oil is one of the most commonly used oils in artistic paints.⁴² Safflower oil is a semidrying oil due to its relatively lower content of unsaturations.²⁷ In modern times, it has been introduced into manufactured oil paints,² synthetic air-drying binders (e.g., alkyd resins), and solvent-borne and WB formulations.¹ In fact, due to the low linolenic acid content, it tends to yellow less than oils with a similar iodine value.²⁷

As a paint system involves the presence of a pigment together with the film former, we started our study by selecting two historically and artistically relevant pigments with different effects on the oil curing: lead white (LW) and synthetic ultramarine blue (UB). LW has been historically the most important of all white pigments⁴³ and the most common is a synthetic pigment⁴⁴— $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$.⁴³ Lead, in lead-based pigments, reacts with acidic moieties in oil paints to form RCOO-Pb-OOCR bonds, which are believed to make the paint more durable by increasing the cross-linking density.^{37,45} Lead ions act as through driers,²¹ which are able to efficiently catalyze the paint curing and accelerate oxygen uptake and autoxidation.^{21,28,46} Synthetic UB is a sulfur-containing sodium aluminum silicate. Its general formula is $(\text{NaCa})_8[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{SO}_4, \text{S}, \text{Cl})_2$,⁴³ and the deep blue color of the pigment is due to the sulfur-containing radical anions inside the aluminosilicate framework.⁴⁷ When synthetic ultramarine is mixed with a drying oil, the oil film dries slowly.⁴² Paint layers with synthetic UB may present a degradation issue, the “ultramarine sickness”, which results in a gray appearance and a loss of detail in the artwork.⁴⁸

Via a free radical process, synthetic UB photocatalyzes the degradation of the oil binder when UV radiation is present,³⁶ and both natural and synthetic UB can act as aluminosilicate catalysts.⁴⁹ UB also catalyzes the photodegradation of polyethylene when added as a pigment.^{50,51} Burnstock et al. reported that ultramarine paint layers in modern oil paintings often present an important conservation issue: the paint is disrupted when saliva and water are used in the cleaning practice.³⁵ This phenomenon, called water sensitivity, has been

hypothesized to be related in some cases to the lack of a well cross-linked oil network.^{10,32}

In this study, a multianalytical methodological approach was implemented to systematically characterize the conversion of the liquid oil paint into a dry film by monitoring the formation of radical species, the reactions taking place with oxygen, and the consequent formation of new molecules.

Our approach is based on isothermal thermogravimetric (TG) analysis to study the kinetics of the oil oxidation and estimate the oxidative degradation, differential scanning calorimetry (DSC) to monitor the presence of hydroperoxides and active radicals over time and to evaluate the stability of peroxides formed in the paint layers, gas chromatography–mass spectrometry (GC–MS) to investigate the noncovalently cross-linked fractions, and analytical pyrolysis coupled with gas chromatography and mass spectrometry (Py–GC–MS) to characterize the whole organic fraction of the model paintings, including the cross-linked network. The model paintings were analyzed periodically over the course of 2 years with a variable frequency depending on the technique and the stage of curing of the paints.

The final aim is to improve our understanding of the curing of artistic air-drying oil paints, the phenomena that occur in a paint film over time and to correlate them to the characteristics and stability of the paint film.

2. EXPERIMENTAL SECTION

2.1. Reagents. Methanol and water were purchased from Sigma-Aldrich (purity 99%). Lauric acid, suberic acid, myristic acid, azelaic acid, sebacic acid, palmitic acid, oleic acid, stearic acid, and tridecanoic acid were purchased from Sigma-Aldrich (purity 99%). Hexadecane acid isooctane, acetone, diethyl ether, and *n*-hexane were purchased from Sigma-Aldrich (high-performance liquid chromatography grade). *N,O*-Bis(-trimethylsilyl)-trifluoroacetamide with 1% trimethylchlorosilane (purity 98.5%) and 1,1,1,3,3,3-hexamethyldisilazane (HMDS) (purity 99.9%) were purchased from Sigma-Aldrich.

2.2. Samples. Linseed oil and safflower oil were purchased from Maimeri (Milano, Italy). Synthetic UB and LW were purchased from Ferrario (Bologna, Italy) and Kremer (Germany), respectively. The systems analyzed in the present study were model oil paints and paintings created in the laboratory. *Oil paints* were prepared by mixing weighted amounts of drying oil and powdered pigment to obtain a workable impasto. Each oil paint was then used to prepare model *oil paintings*, casting the oil paints onto glass slides. The oil paintings were thus left to dry and cure under indoor laboratory conditions. Table 1 reports the detailed description of the oil paints.

Table 1. Description of Oil Paints

oil paints	pigment	(%)	oil	(%)
LWLO	LW	66	linseed oil	34
UBLO	UB	61	linseed oil	39
LWSO	LW	77	safflower oil	23
UBSO	UB	49	safflower oil	51

2.3. Drying Time. Paint drying, and in particular set-to-touch, dry-to-touch, and dry-hard-time, were measured according to ASTM D1640: standard test methods for drying, curing, or film formation of organic coatings at room temperature. The paints were cast on a glass slides to produce a homogeneous 0.45 mm wet film.

2.4. Thermogravimetric Analysis. A TA-Instruments thermobalance, model Q5000IR, was used for TG investigations and determination of the oxygen uptake under a constant air flow (25 mL/min) at 80 °C for 3000 min (2 days). The sample masses ranged between 6 and 9 mg. Temperature calibration was based on the Curie point of paramagnetic metals. A multipoint calibration with 5 Ci

points from reference materials (Alumel, Ni, Ni 83% Co 17 %, Ni 63% Co 37%, and Ni 37% Co 63%) was performed. The oxygen uptake curves of the oil paints were normalized to the oil content. The fitting of the oxygen uptake curves was performed with the software OriginPro8.

2.5. Differential Scanning Calorimetry. DSC analyses were performed with a differential scanning calorimeter, Mettler Toledo DSC8222e, under constant nitrogen flow (80 mL/min) in the 30–300 °C temperature range, with a 10 °C/min heating rate. Samples (4–6 mg) were scratched from the cast of oil paint and placed in aluminum pans. DSC curves of the oil paint models were normalized to the oil content. Temperature and heat flow were calibrated using indium. The baseline was calibrated using two empty aluminum pans.

2.6. Gas Chromatography–Mass Spectrometry. For the GC–MS calibration, standard solutions of lauric acid (4.88 ppm), myristic acid (4.83 ppm), palmitic acid (4.95 ppm), oleic acid (4.78 ppm), stearic acid (4.97 ppm), azelaic acid (4.82 ppm), suberic acid (4.93 ppm), and sebacic acid (4.88 ppm) were prepared in acetone. Tridecanoic acid and hexadecane were used as internal standards for derivatization and injection. The samples' weight ranged between 0.3 and 0.6 mg, and they were subject to alkaline hydrolysis, followed by acidification, extraction with an organic solvent, silylation, and GC–MS analysis. Details are reported elsewhere.⁵² A gas chromatograph 6890 N GC system (Agilent Technologies, Palo Alto, CA, USA) coupled with a 5975 Mass Selective Detector (Agilent Technologies, Palo Alto, CA, USA) single quadrupole mass spectrometer was used. For the gas chromatographic separation, an HP-5ms fused silica capillary column (5%-diphenyl/95%-dimethyl polysiloxane, 30 m, 0.25 mm i.d., 0.25 mm film thickness (J&W Scientific, Agilent Technologies, Palo Alto, CA) with a deactivated silica precolumn (2 m, 0.32 mm i.d., J&W Scientific Agilent Technologies, Palo Alto, CA) was used. The PTV injector was used in split-less mode at 280 °C. The carrier gas was used in the constant flow mode (He, purity 99.995%) at 1.0 mL/min. The chromatographic oven was programmed as follows: initial temperature 80 °C, isothermal for 2 min; 10 °C/min up to 280 °C, and isothermal for 30 min. The MS transfer line temperature was 280 °C, the MS ion source temperature was 230 °C, and the MS quadrupole temperature was 150 °C. The mass spectrometer operated in electron impact (EI) positive mode (70 eV) with a scan range m/z 50–700. MS spectra were recorded both in TIC (total ion current) and single ion monitoring mode. Experiments were performed in triplicate.

2.7. Analytical Pyrolysis Coupled with Gas Chromatography and Mass Spectrometry. The instrumentation consisted of a microfurnace multishot pyrolyzer EGA/Py-3030D (Frontier Lab) coupled to a gas chromatograph 6890 (Agilent Technologies, Palo Alto, CA, USA) and to an Agilent 5973 Mass Selective Detector operating in EI mode at 70 eV. The split/split-less injector was used in split mode at 280 °C, with a split ratio 30:1. The chromatographic conditions were as follows: 50 °C isothermal for 2 min, 10 °C/min up to 280 °C and isothermal for 2 min, and 15 °C/min up to 300 °C and isothermal for 30 min. The carrier gas (He, purity 99.9995%) was used in the constant flow mode at 1.0 mL/min. The temperatures of the MS transfer line, MS ion source, and MS quadrupole were 280, 230, and 150 °C, respectively. The mass spectrometer was operated in EI positive mode (70 eV) with a scan range m/z 50–600. MS spectra were recorded in TIC mode. A total of 300 µg of the sample was placed in a pyrolysis cup and admixed to 5 µL HMDS used as a silylating agent for the in-situ derivatization of pyrolysis products. Analyses were performed in triplicate.

3. RESULTS

3.1. Drying Time. The drying time of the model paintings were measured according to the ASTM D1640 method. Set-to-touch, dry-to-touch, and dry-hard-time data are reported in Table 2.

As expected, for both oil binders, LW-based paint layers dry faster than those based on UB. Also, for both pigments,

Table 2. Set-to-Touch-Time (TSTT), Dry-to-Touch-Time (TDTT), and Dry-Hard Time (TDH) in Hours of Model Paintings

model oil paint	TSTT (h)	TDTT (h)	TDH (h)
LWLO	63	90	134
UBLO	213	242	284
LWSO	112	157	207
UBSO	234	261	305

safflower oil-based paint layers dry slower than those based on linseed oil.

3.2. Thermogravimetric Analysis. The oil curing under accelerated conditions was followed by TG analysis. Fresh oils and paints were cured at 80 °C for 3000 min in a thermobalance under airflow, and the oxygen uptake curve was registered (Figures 1, S1, and S2 in the Supporting Information). The temperature was chosen to ensure reasonable analysis time, as done in other works.^{8,53–55} Although artistic paint layers do not normally cure at 80 °C, the method is a valid tool to compare in a highly reproducible way the oxidative behavior of the different oil paints. Curves up to 500 min are shown in Figure 1.

All the paints show a rapid oxygen uptake in the first 2 h, with a mass increase in the range 3–7% due to the initial addition of oxygen (Figures 1, S1, and S2 in the Supporting Information).^{8,52,55} The mass increase is followed by a region where a mass loss is evident due to the decomposition of oxygenated compounds formed, with the evolution of relatively low-molecular weight molecules.^{8,56} The curve shape is a balance between the two phenomena, and for this reason, its visual investigation does not allow a straightforward comparison between the different paints. To address this, we propose here eq 1 as a qualitative and descriptive equation for the oxygen uptake profiles.

$$\text{Mass } \% (t) = \frac{A \cdot [q \cdot e^{-\lambda_1 t} + (1 - q) \cdot e^{-\lambda_2 t}]}{1 + e^{-\lambda_0(t-t_0)}} + B \quad (1)$$

(A , B , q , λ_i , t_0 fitting parameters). Although eq 1 is intended as a qualitative and descriptive equation, it should reflect the kinetics of the overall process and the parameters therein should be interpreted accordingly. The use of this equation implicitly assumes that each of the processes involved in the oxygen uptake profiles is a first-order (or pseudo-first-order) process. Under non-limiting oxygen conditions, as in our experiments, the oxygen consumption is defined as a pseudo-first-order reaction with respect to the substrate concentration.^{57,58} The mass increase ascribed to the oxygen addition is hence described by a sigmoidal function $1/[1 + e^{-\lambda_0(t-t_0)}]$, which also allows to account for an induction time (if present). The two other exponential processes ($e^{-\lambda_1 t}$ and $e^{-\lambda_2 t}$) are relative to mass losses. The mass loss can be associated with the evolution of different molecules including aldehydes and ketones and is generally ascribed to the exponential decomposition of hydroperoxides.^{59,60} A descriptive equation with only one exponential to describe the mass loss was also tried but did not prove satisfactory (Figure S1 in Supporting Information). The meaning of the parameters should be as follows:

- A is the overall mass loss
- B is the asymptote of mass % curve for t that tends to infinity

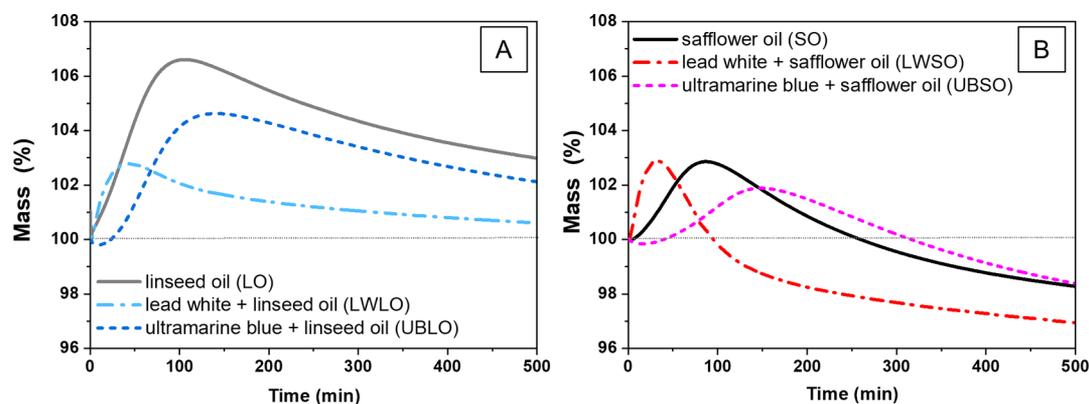


Figure 1. Oxygen uptake curves vs time of model oil paints. Curves are recorded under air flow at a constant temperature of 80 °C, and data are normalized for the oil content. (A) LO (solid gray line), LWLO (dashed and dotted light-blue line) and UBLO (dashed blue line); (B) SO (solid black line), LWSO (dashed and dotted red line), and UBLO (dashed pink line).

Table 3. Values of Parameters and Their Standard Error in Brackets; X^2 and R^2 Coefficients Obtained by Fitting the Oxygen Uptake Profiles with eq 1 for LO, LWLO, UBLO, SO, LWSO, and UBLO

model paints	A	B	C	q	$\lambda_0 \times 10$ (min ⁻¹)	$\lambda_1 \times 10^2$ (min ⁻¹)	$\lambda_2 \times 10^4$ (min ⁻¹)	t_0 (min)	$X^2 \times 10^3$	R^2
LO	10.813 (0.004)	98.576 (0.003)	9.25	0.599 (<0.001)	0.450 (<0.001)	0.392 (<0.001)	4.36 (0.01)	40.3 (<0.1)	0.34	0.99987
LWLO	5.659 (0.004)	97.836 (0.002)	3.47	0.399 (<0.001)	1.104 (0.003)	0.780 (0.002)	4.71 (0.01)	5.8 (<0.1)	0.60	0.99933
UBLO	9.62 (0.01)	98.079 (0.005)	7.18	0.571 (0.001)	0.328 (0.001)	0.367 (0.001)	5.13 (0.02)	62.4 (0.1)	1.33	0.99938
SO	12.61 (0.02)	95.331 (0.002)	7.32	0.728 (<0.001)	0.299 (0.001)	0.630 (0.001)	6.20 (0.02)	26.4 (0.1)	1.49	0.99935
LWSO	15.31 (0.03)	91.974 (0.004)	7.28	0.597 (<0.001)	0.798 (0.005)	1.500 (0.005)	4.95 (0.01)	0.9 (0.1)	3.86	0.99888
UBSO	20.90 (0.20)	94.057 (0.004)	13.63	0.776 (0.001)	0.128 (<0.001)	0.594 (0.003)	6.08 (0.02)	87.3 (0.8)	3.98	0.99881

- λ_0 is the apparent time constant for the oxygen uptake process
- λ_1, λ_2 are the apparent time constants for the two main mass loss phenomena
- $q, (1 - q)$ are the relative weights of the two relevant processes that are responsible for the mass loss
- t_0 is the abscissa of the inflexion point of the sigmoidal function related to the induction time of the oxygen uptake process

The fitting parameters obtained are reported in Table 3 and the fitted curves in Figure S2 in the Supporting Information.

3.2.1. Mass Uptake. λ_0 and t_0 values show that LW catalyzes the mass uptake both in linseed oil—in agreement with previous observations^{28,46}—and safflower oil, as the apparent time constants are both about one order of magnitude bigger than those of the corresponding oils alone, and t_0 values are one order of magnitude smaller. As far as UB-based paints are concerned, the one with linseed oil presents a similar apparent time constant and the same order of magnitude but the bigger value of t_0 , with respect to the oil alone, indicating that UB causes a small acceleration of the oxygen uptake in linseed oil. UBLO paint is the one that presents the lowest apparent time constant (1 order of magnitude smaller than the oil alone) and the biggest t_0 , resulting in the paint with the slowest oxygen uptake.

The C parameter in Table 3, estimated as $C = A \cdot [q \cdot e^{(-\lambda_1 t_{\text{onset}})} + (1 - q) \cdot e^{(-\lambda_2 t_{\text{onset}})}]$, allows us to estimate the mass of oxygen taken by the paint with time, without taking into consideration

further reactions. If we compare the oils alone, LO and SO show similar values, with LO being slightly bigger than SO, in agreement with the iodine numbers of these oils.⁶¹ Things change significantly when pigments are added. LW halves the amount of oxygen that is added to linseed oil, while very similar values are obtained in the case of safflower oil. UB reduces, although of a lower extent than LW, the amount of oxygen added to linseed oil but doubles the amount of oxygen added when safflower oil is concerned. Oxygen adds to alkyl radicals formed upon hydrogen abstraction, with formation of peroxy radicals. Oxygen is also added in other possible reactions, including *internal rearrangement*, *addition to double bonds*, and *recombination of peroxy radicals*.¹⁰ The fact that LW reduces the amount of oxygen taken by the oil can be interpreted as a consequence of the evolution of unsaturated fatty acids through other reaction pathways—cross-linking—and a low occurrence of the abovementioned reactions of peroxy radicals.¹⁰ UB on the other hand, adds always more oxygen than LW (double), and in the case of safflower oil, also more than the oil alone. We can interpret this as a result of low evolution of polyunsaturated fatty acids through cross-linking and a high degree of oxidation.¹⁰

3.2.2. Mass Loss. The scission of alkoxy radicals deriving from the peroxidation of unsaturated triglyceride fatty acids has been long discussed, and it leads mainly to the formation of hydrocarbons, furans, and oxo- and hydroxy-fatty acids with a shorter chain length.^{6,14,62} Among these, several are volatile molecules, and many of them can also further react to produce

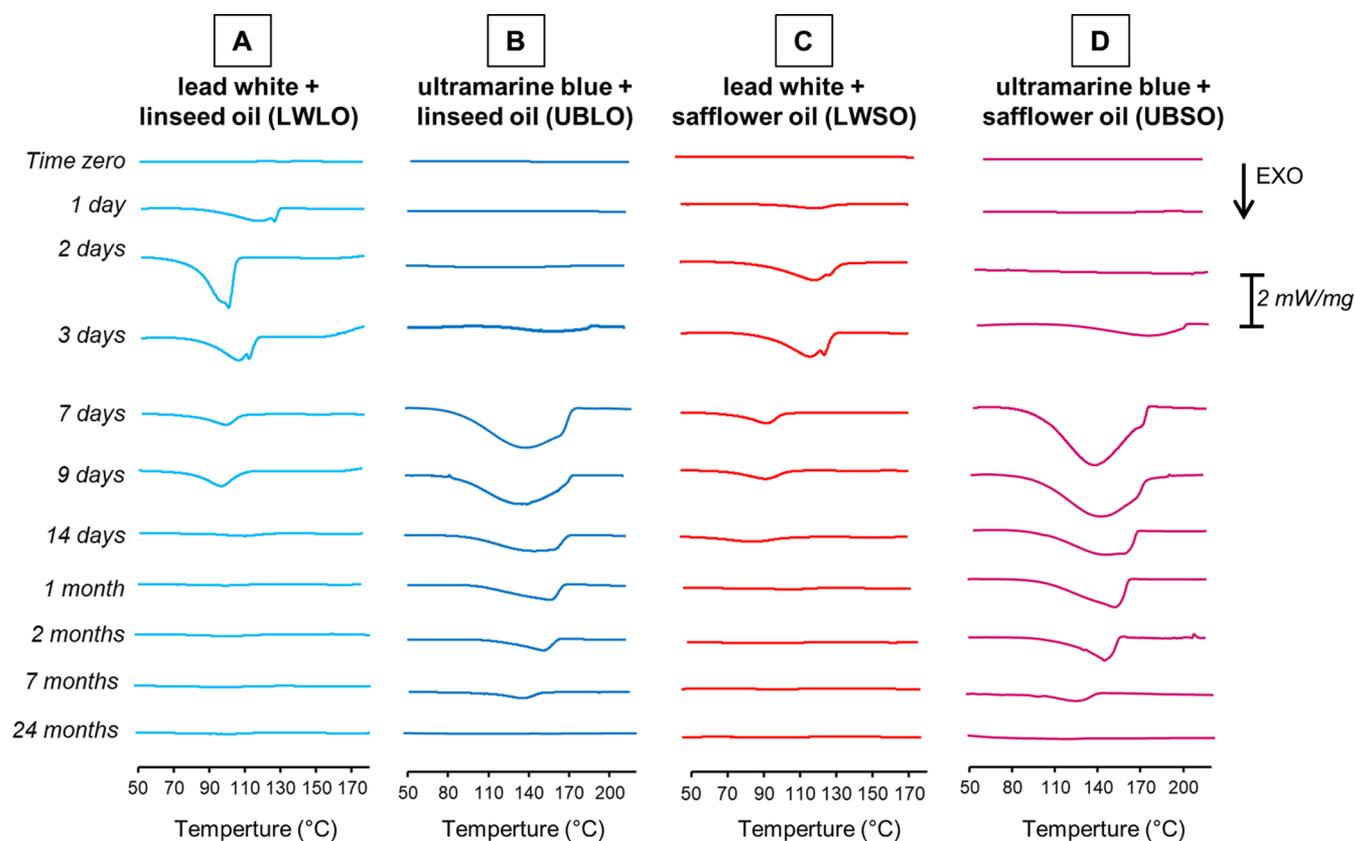


Figure 2. DSC curves—normalized to the oil content—of model oil paintings recorded up to 24 months of natural aging. (A) LWLO (light blue line); (B) UBLO (blue line); (C) LWSO (red line); (D) UBSO (pink line).

Table 4. Onset Temperature T_{onset} (°C) and Maximum Temperature T_{peak} (°C) Extrapolated from DSC Curves vs Curing Time of Model Oil Paintings

	LWLO		UBLO		LWSO		UBSO	
	T_{onset} (°C)	T_{peak} (°C)						
1 day	95	119			99	129		
2 days	90	127			95	127		
3 days	95	116	108	162	97	125	115	171
7 days	91	108	92	141	87	107	97	138
9 days	91	114	88	140	76	98	85	144
14 days	91	111	97	149	69	91	97	144
1 month			100	161			103	154
2 months			110	155			118	146
3 months			125	147			114	136
4 months			122	142			112	142
5 months			120	142			110	132
6 months			117	139			108	129
7 months			102	136			105	125
24 months								

other oxo- and hydroxy-fatty acids with a shorter chain length.^{6,14,62}

The fitting clearly shows that there are two phenomena (1 and 2) which are responsible for a mass loss, and each phenomenon must be intended as a combination of reactions which lead, among other things, to the formation of low-molecular-weight molecules. The two mass loss phenomena—1 and 2—are, respectively, the fastest and the slowest one. In the case of LW with linseed oil, the first mass loss phenomenon has a smaller weight than the second one (q), meaning that the mass loss occurring because of the first phenomenon leads to a

smaller mass loss than the one due to the slower phenomenon. The opposite is true for all other paints.

The A values represent the total mass loss, observed as a consequence of both 1 and 2 phenomena. As the mass loss is a consequence of oxidative degradation,⁸ which competes with cross-linking, a higher mass loss can be used as an index of a higher extent of lipid oxidation, as opposed to the lipid cross-linking. LW with linseed oil is the paint with the lowest mass loss. UB causes a higher mass loss in all paints, and SO-based paints have always a higher mass loss than LO-based paints.

Table 5. Characteristic Parameters Relative to Samples from Model Oil Paintings Analyzed by GC–MS after 7 and 24 Months of Natural Aging^a

	P/S		A/P		O/S		Σ Dic. %	
	7 m	24 m	7 m	24 m	7 m	24 m	7 m	24 m
LWLO	1.1 ± 0.0	1.6 ± 0.2	2.0 ± 0.0	2.1 ± 1.0	0.0 ± 0.0	0.0 ± 0.0	53.0 ± 5.6	58.7 ± 11.7
UBLO	1.3 ± 0.1	1.7 ± 0.2	3.0 ± 0.5	1.8 ± 0.8	0.0 ± 0.0	0.0 ± 0.0	63.7 ± 3.8	56.3 ± 9.6
LWSO	2.2 ± 0.4	3.0 ± 1.2	6.1 ± 1.0	1.3 ± 0.1	0.1 ± 0.1	0.1 ± 0.0	81.1 ± 1.5	52.6 ± 2.8
UBSO	2.0 ± 0.4	3.4 ± 1.1	3.1 ± 1.1	0.4 ± 0.1	0.1 ± 0.1	0.0 ± 0.0	67.4 ± 8.5	34.5 ± 9.4

^aConfidence intervals are reported, calculated at 95% confidence level. P/S: palmitic acid (hexadecanoic) to stearic acid (octadecanoic) ratio, A/P: azelaic acid (nonanedioic acid) to palmitic acid ratio, O/S: oleic acid ((9Z)-octadec-9-enoic acid) to stearic acid ratio, Σ Dic. %: sum (%) of the dicarboxylic acids – suberic acid (octanedioic acid), azelaic acid, and sebacic acid (decanedioic acid).

3.3. Differential Scanning Calorimetry. The curing of the oil paints was monitored by DSC with a dynamic method under a nitrogen flow.^{8,63,64} DSC analyses were performed on samples collected from the model paintings, starting from the time zero (t_0) and then on regular time intervals up to 24 months (see Figures 2, S3 and S4 in the Supporting Information). Table 4 shows the extrapolated onset temperature (T_{onset}) and the maximum temperature (T_{peak}) of the DSC profiles acquired. An endothermic effect above 200 °C was observed in the LW paint layers, due to pigment decomposition, but was not recorded as it was not relevant to this study.

At the beginning, no signals were observed until the formation of peroxides and radical species occurred, at which point an (overall) exothermic heat effect appeared and changed with the sample age. The exothermic effect is due to different overlapping phenomena: the decomposition of peroxides and hydroperoxides, which is endothermic, and the recombination of radical species—those deriving from the peroxides and hydroperoxides decomposed, as well as other radicals species present in the paint film (such as R[•], RO[•], and ROO[•])—which is exothermic.^{55,63,64} The area of the peak recorded is thus proportional to the sum of the number of broken peroxide bonds and free radical species present in a sample at a given time. When the exothermic signal decreases to almost zero, we can assume that the concentration of the active species is very low.^{63–65} This does not necessarily mean that the chemical drying is complete, as double bonds might still be present, and thus susceptible to further reactions. In the temperature range observed, the evaporation (endothermic effect) of small volatile oxygenated products of oxidation can also be observed at higher temperatures, if not superimposed to the main exothermic peak.

The DSC curves of LW containing paint layers show similar shapes, and an exothermic heat effect in the temperature range 90–130 °C for LWLO and 70–135 °C for LWSO is observed. The maximum intensity is reached after 2 days in LWLO and after 3 days in LWSO (Figure 2A,C and Table 4). The DSC curves of UB containing paint layers show similar shapes and an exothermic broader heat effect in the temperature range 70–190 °C, starting after 3 days and reaching the maximum value after 7 days (Figure 2B,D and Table 4). The delay in the peak appearance in UB-based paints confirms the results on the catalytic effect of LW and the retardant effect of UB on peroxide radical formation observed in the oxygen uptake curves.

The T_{onset} of the peak, indicating the starting temperature of peroxide decomposition, follows the trend: T_{onset} (LWLO) < T_{onset} (LO) < T_{onset} (UBLO) and T_{onset} (LWSO) < T_{onset} (SO) < T_{onset} (UBSO) (Figures S3 and 2, Tables 4, S1 and S2 in the

Supporting Information). The DSC nonisothermal measurement can assess the thermal stability of the peroxides resulting from autoxidation.⁶⁵ The trend of T_{onset} values indicates that LW leads to the formation of less stable peroxides, while UB to more stable ones (Table 4).

Under experimental conditions adopted, active species (peroxides and free radicals) could not be detected after almost 2 months in LW-based paint layers, while for UB ones, a calorimetric signal was still present after 7 months. This indicates a catalytic effect of LW and a retardant effect of UB also on the cross-linking. This retardant effect of UB can also be linked to the observed stabilization of the peroxides operated by the pigment. The decomposition of hydroperoxides is considered to be the key rate-limiting step based on the fact that it is the only propagation step involving any significant activation energy.¹² If a peroxide is stabilized by UB, the activation energy for its decomposition becomes higher, and other reaction pathways^{10,13,14} might become predominant.

3.4. Gas Chromatography–Mass Spectrometry. GC–MS analyses were performed at 7 and 24 months of natural aging, after saponification, hydrolysis, and derivatization, to investigate the fractions of the oil phase noncovalently cross-linked (through C–C and C–O–C bonds). The TICs (total ion chromatograms) are reported in Figures S5, S6, S7, and S8 in the Supporting Information. The compounds identified are listed in Table S3. Quantitative analyses of mono- and dicarboxylic acids were performed, and data are reported in Table 5.

Most relevant, after 24 months of natural aging is the fact that in safflower-based paints, the relative content of azelaic acid is significantly decreased with respect to the values recorded after 7 months. To the best of our knowledge, this is the first time that such a decrease is observed. Azelaic and other dicarboxylic acids, formed by oxidation of (poly)-unsaturated fatty acids, are considered final products of oxidation.²⁴ The data presented here clearly demonstrate that they are not, and there must be reaction pathways that lead to their decomposition into other reaction products. Such products were not identified in the chromatograms. A possible explanation is that these compounds, due to their low molecular weight, might have retention times lower than the solvent delay of the chromatographic run. Another possible explanation is that dicarboxylic acids might become covalently bound (through C–C and C–O–C bonds) to the cross-linked network. The fact that such decrease was not observed for linseed oil paints might mean that these reactions do not take place in linseed oil to a significant extent or that we have missed the point where the relative content of dicarboxylic acids reached a maximum and then decreased, which must

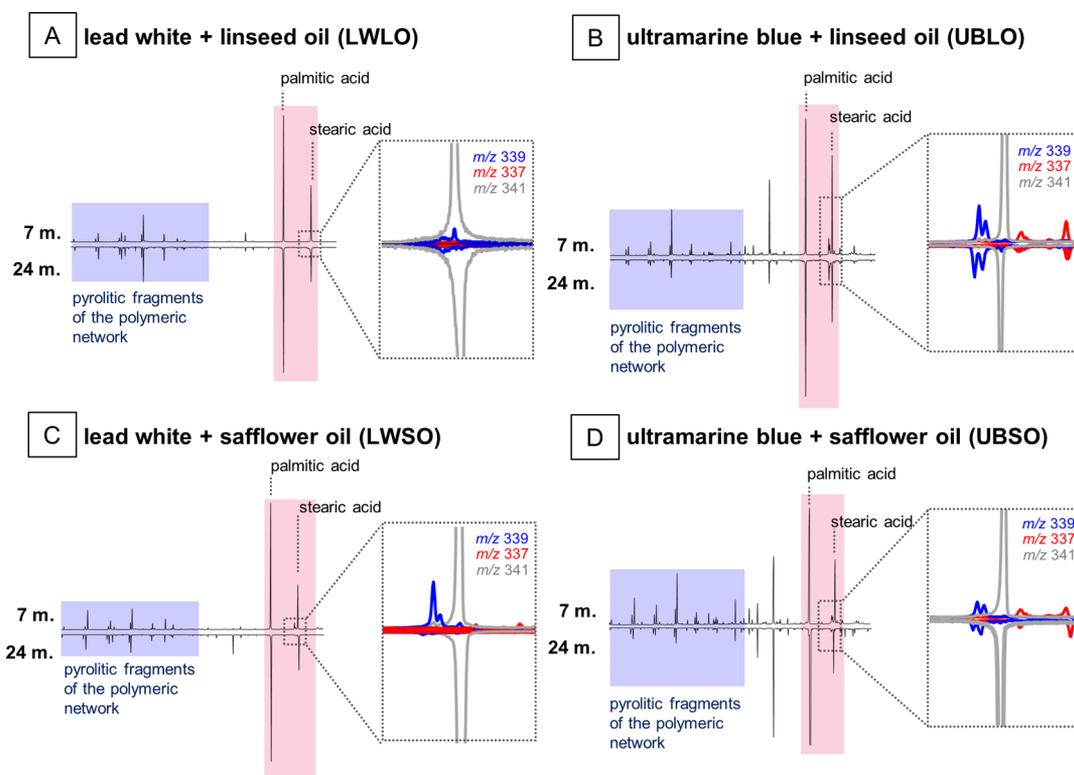


Figure 3. Extracted ion pyrograms of m/z 129 of model oil paintings after 7 (7 m) and 24 months (24 m) of natural aging. In the insets, the chromatographic profiles of unsaturated fatty acids are reported. m/z 339: octadecenoic acid (oleic acid), m/z 337: octadecadienoic acid (linoleic acid). As reference, the extract ion of octadecanoic acid (stearic acid) is reported (m/z : 341). (A) LWLO; (B) UBLO; (C) LWSO; (D) UBSO.

have occurred before 7 months. Considering the faster kinetics of curing of linseed oil-based paints, this hypothesis is not to be excluded.

Hydroxyacids—intermediate products of oxidation⁵²—were investigated and detected in all chromatograms and were identified by mass spectral interpretation and by comparison with the available literature.⁶⁶ α -Hydroxyacids and α -hydroxy di-acids ranging from 5 to 10 carbon atoms were detected both after 7 and 24 months in all samples (chromatographic profiles in Figures S5–S9, and Table S3, and mass spectra Figure S9–S18 in the [Supporting Information](#)). The formation of α -hydroxyacids and α -hydroxy di-acids ranging from 5 to 10 carbon atoms could be justified as the consequence of oxidation of double bonds followed by β -elimination, given the position of double bonds in oleic, linoleic, and linolenic acids.⁷ α -Hydroxy hexadecanoic and α -hydroxyl octadecanoic acid (mass spectra in Figures S19 and S20 in the [Supporting Information](#)) were only detected at 24 months of natural aging. Their formation can only be ascribed to the oxidation of palmitic and stearic acid in position α and have never been reported, to the best of our knowledge, in the context of curing and autoxidation of glycerolipids.

3.5. Analytical Pyrolysis Coupled with Gas Chromatography and Mass Spectrometry. Py–GC–MS enabled the investigation of the whole organic fraction of the paints, including the cross-linked network. The extracted ion chromatograms of m/z 129 ascribable to silylated carboxylic acid moieties obtained at 7 and 24 months of natural aging are shown in [Figures 3](#) and [S21](#). The complete list of the identified compounds is reported in [Table S3](#).

Pyrolytic profiles are strongly affected by the pigment nature.^{25,67} It is thus in general not possible to compare

pyrograms of samples containing different pigments, but the comparison between chromatographic profiles of samples collected from the same paint layers at different stages of aging is still possible. Short-chain linear carboxylic acids, saturated and ω -unsaturated, ranging from 6 to 12, and peaking at 8, are the products of pyrolysis of the cross-linked network.⁵⁵ LW-based paints at both 7 and 24 months of natural aging are quite similar, and only a slight increase in the relative intensity of the peaks ascribable to the pyrolysis of the cross-linked network is observable at longer curing times ([Figure 3A,C](#)). This suggests that the relative content of the cross-linked network is relatively increased with time, as expected of a curing oil paint film. The opposite, though, is observed in UB-based paints ([Figure 3B,C](#)), suggesting that the degradative oxidation of the cross-linked network is taking place.

In the pyrogram of UBLO, LWSO and UBSO unsaturated compounds were detected: high amounts of oleic acid—which is significantly higher than in GC–MS chromatogram; *trans*-octadec-9-enoic acid; 8-hydroxydec-9-enoic acid; 8-hydroxyundec-10-enoic acid; and 9-hydroxyoctadec-12-enoic acid (the molecular structure was tentatively assigned based on the mass spectra reported in [Figure S22](#) in the [Supporting Information](#)). Given their absence in the GC–MS chromatograms, these compounds must be ascribed to the pyrolysis of (unsaturated fatty) acids covalently bound (through C–C and C–O–C bonds) to the cross-linked network. UBLO and UBSO paints both present a thermal effect still after 24 months of curing, but LWSO did not present any thermal effect after 2 months (see DSC results and [Figure 2](#)). This confirms that although active radical species may be very low in abundance

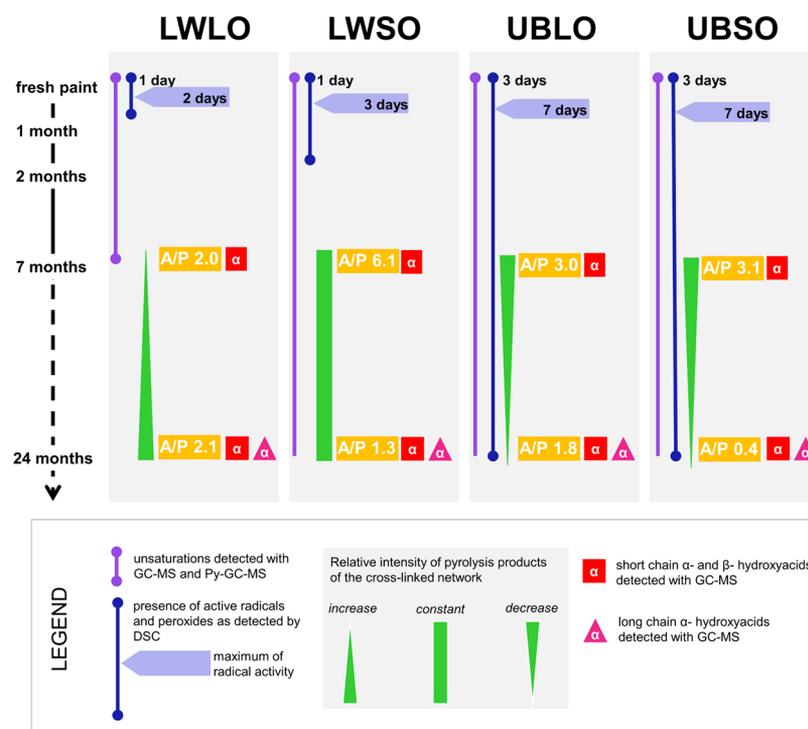


Figure 4. Summary of the principal results obtained in the study.

in paint layers, unsaturations may still be still present, available for further reactions.

4. DISCUSSION

A scheme to summarize the principal findings is reported in Figure 4.

The thermal behavior of the paints and molecular profiles of the painting layers clearly confirm that the curing of oil paints is dependent on both the type of oil and the pigment.

Safflower oil, which is considered a semidrying oil, shows a very different behavior with respect to linseed oil. Oxidative degradative phenomena start earlier, and they are faster. Safflower oil is also more subject to reaction pathways lead by peroxy radicals, which favor oxidation.^{13,14} All these features can be correlated to the reactivity of bis-allylic positions and their lower content in linolenic acid—the main fatty acid in safflower oil, compared to linolenic acid—the main fatty acid of linseed oil.¹⁰

In a painting layer containing LW, after 7 months of natural curing, most active species are absent, or present at very low concentrations, especially in linseed oil-based paintings. It is well known that LW is a through drier, which catalyzes both the initiation and autoxidation in an oil paint.²⁸ TG and DSC data in the present study show that LW catalyzes the oxygen uptake to form peroxides—the initiation step of autoxidation reactions, in agreement with the observed behavior of other primary and through driers,^{28,54} as well as the cross-linking and volatile formation and evolution. We showed for the first time that LW decreases the stability of the peroxides (DSC). This can be directly linked to the catalytic effect of LW both in the cross-linking reaction and volatile formation. All techniques used show that the effect of LW on the reactivity of polyunsaturated triglyceride fatty acids is oil-dependent, and double bond consumption is faster when a drying oil is used.

Synthetic UB was shown in this study to have a retardant effect on the oxygen uptake and radical peroxide formation respect with the oils alone and LW-based paints (TG and DSC). UB was proven to stabilize the peroxides formed upon oxygen uptake (DSC), affecting the curing kinetics and, possibly favoring alternative reaction pathways with respect to those typical of autoxidation reactions.^{10,13,14} UB-based paint films are subject to a higher degree of oxidation than LW-based ones (GC-MS); the formation and evolution of volatile compounds are slower and continue for a longer time (TG, DSC), competing with the formation of a stable cross-linked network. This is also evident by analyzing the pyrolysis data, which show that the cross-linked network of UB model painting gets degraded with time, most likely to the advantage of oxidative degradation reactions. This observation is in agreement with the work of de la Rie et al.,³⁶ which demonstrated the physical disruption of the oil binder UB-based paintings upon light aging. Moreover, it strongly supports the hypothesis that synthetic UB paint layers may commonly present water sensitivity, caused by a poorly established cross-linked network, and the presence of relatively high amounts of polar oxidized (relatively low molecular weight) species.^{10,32}

Mass spectrometric data show that dicarboxylic acids formed upon curing (in safflower oil-based paints) reach a maximum and then decrease (GC-MS). Moreover, short α -hydroxy dicarboxylic acids (from 8 to 10 carbons) were detected both at 7 and 24 months of natural aging, and α -hydroxy hexadecanoic and octadecanoic acids were detected at 24 months of natural aging. This proves that oxidation in alpha to the carbonyl moiety can take place upon curing. These data are extremely interesting, as they confirm the hypothesis^{10,13,14} that the reaction pathways involved in the curing of a drying oil are much more than those reported in the literature and include several possible paths for oxidative degradation,

including the progressive oxidation of fatty acids in position α to the carbonyl moieties. This phenomenon has never been observed before, although recently, the hypothesis that the position α to the carbonyl moiety might be susceptible to oxidation in glycerolipids has been advanced, in relation to the formation, upon further oxidation, of oxalic acid.¹⁰ Insoluble salts of oxalic acid are largely detected in aged oil paintings,^{68,69} also in association with UB paints.⁷⁰ The presence in the painting films of α -hydroxyl hexadecanoic and octadecanoic acids, strongly supports this hypothesis, as further oxidation of the hydroxyl moiety would lead to oxoacetic acid, and, ultimately, to oxalic acid. Oxidation of carboxylic acids in alpha to carboxylic moieties upon curing contradicts two common assumptions normally made in the molecular analysis of artists' oil painting layers. The first is that saturated fatty acids as palmitic and stearic acids are stable and are thus not subject to any reaction in the formation of a mature oil paint film (besides metal soap formation). The second is that the azelaic-to-palmitic acid ratio is as an index of the degree of oxidation of an oil paint.

5. CONCLUSIONS

In this study, a multianalytical approach was implemented in order to investigate the curing and maturing of air-drying artistic oil paints during 24 months of natural aging. The final aim is to improve our understanding of the curing of artistic air-drying oil paints, the phenomena that may take place in a paint film with time, and try to correlate them to the paint film characteristics and stability. The study was carried out on model paints based on linseed oil (a drying oil) and safflower oil (a semidrying oil) with two different pigments: LW, a through drier, and UB, which has been often correlated with degradation phenomena of modern oil paintings.

When in a painting layer, an oil—both drying and semidrying oil, is mixed with LW, the oil mobile phase converts quickly in a well cross-linked network and presents a relatively low degree of oxidation. Painting layers containing synthetic UB show a very different behavior, especially when a semidrying oil is used. On the whole, it is clear that increased levels of oxidative degradation occur in synthetic UB paintings in comparison to LW ones and significantly the more so when UB is used in combination with safflower oil. As a result, we can expect that an UB painting layer is less cross-linked than a LW-based one when other factors (oil type, additives, age, conservation conditions, etc.) are the same.

This tendency of UB to favor oxidative degradation over cross-linking may be related to documented conservation issues of ultramarine painting layers, from the loss of cohesion to the establishment of water sensitivity.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsapm.0c01441>.

Experimental and fitted oxygen uptake profiles of linseed oil obtained by the equation with only one exponential and by eq 1; experimental and fitted oxygen uptake profiles of oils and model oil paints by eq 1; DSC curves of oils and model oil paints; T_{onset} , T_{peak} of the normalized DSC curves for oils and model oil paints; list of compounds identified as trimethylsilyl derivatives in the chromatograms obtained by GC–MS and Py–

GC–MS of model oil paints; total ion chromatograms obtained by GC–MS analysis of model oil paints; mass spectra of α - and β -hydroxyacids obtained with GC–MS; extracted ion pyrograms of m/z 129 of model oil paints; and mass spectra attributed to 8-hydroxydec-9-enoic acid, 8-hydroxyundec-10-enoic acid and 9-hydroxyoctadec-12-enoic acid obtained with Py–GC–MS (PDF)

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was performed within the context of the JPI CMOP project: “Cleaning of Modern Oil Paints” (Heritage Plus Joint Call project 2015–2018).

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