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Uncovering the Lead Formate Crystallization in Oil-Based Paintings

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Keywords

Lead oxide, lead formate, oil paintings, pigment-binder interactions, XRPD, ssNMR

Abstract

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Lead carboxylates are an extensive group of compounds studied for their promising industrial applications as well as for their risky behavior when they are formed in oil paintings as corrosion products of lead-based pigments, leading to serious deterioration of paintings. Although the processes leading to the formation of aggregates, protrusions or inclusions, affecting undesirably the appearance of paintings, are assumed to be long-term, the initial stages of the neo-formed lead carboxylates are detectable in the early state of paints' drying. To uncover the chemical changes of lead pigments during the drying of the oil paint films, model systems consisting of minium (Pb_3O_4) and four common drying oils were studied by X-ray powder diffraction (XRPD), ¹³C and ²⁰⁷Pb solid state NMR (ssNMR) and Fourier-transformed infrared spectroscopy (FTIR). For the first time, a degradation mechanism of Pb_3O_4 via the crystallization of lead formate (Pb(HCOO)₂), in the end of the oxidation stage of polymerization of oil paint film, was uncovered. The formation of formic acid in oils was proved by gas chromatography-mass spectroscopy (GC-MS). The vapor experiments evidenced the susceptibility of Pb_3O_4 to react with volatile formic acid released during autoxidation of oils comparably to the direct pigment-binder interactions in paint films. The investigation of the local environment of lead atoms in the paint film by ²⁰⁷Pb WURST-CPMG NMR spectroscopy showed that Pb(II) atoms reacted with linseed oil preferentially to form highly crystalline Pb(HCOO)₂, while the local chemical environment of Pb(IV) atoms did not change. The results proved the co-existence of (i) highly crystalline Pb(HCOO)₂, (ii) highly mobile amorphous phase corresponding to free carboxylic acids or nascent lead soap phase and (iii) remaining Pb_3O_4 in the polymeric/ionomeric network. $Pb(HCOO)_2$ is assumed to be an intermediate for conversion of Pb_3O_4 to lead soaps and/or lead carbonates.

Introduction

Historical paintings have been chemically changing since their creation. While some of these changes only reduce the aesthetic value of the artwork, many of them cause serious damage. Since paint layers represent complicated heterogeneous mixtures of organic and inorganic components, it is difficult to uncover the mechanisms of the degradation processes. These undesirable phenomena, often poorly understood, are influenced by both internal and external factors (e.g., susceptibility of components to environmental conditions). The attention is given especially to the degradation of lead-based pigments, representing on one hand the widespread and extensively used colorants in the history of European art, while on the other hand, being susceptible to numerous reactions with salts or other components in paint layers, they lead to undesirable changes within the paintings.^{1–6}

An example of such phenomena that seriously endangers mechanical cohesion of paint layers is the formation of metal soaps – saponification. Metal carboxylates, being secondary products of reaction between metal ions (typically Pb or Zn from commonly used inorganic pigments) and free fatty acids (FA, released from hydrolyzed triglycerides of oil-based binders), were widely documented in numerous paintings from various historical periods.¹

Resulting in blistering, protruding, spalling or color changes of oil paintings, saponification-related phenomena represent article Online particularly topical problem studied in various scientific fields. The reports contributing to the description of metal carboxylates' transport through paint layers,^{3,4} evaluating the composition and/or crystal structure of metal soaps,⁵ developing new analytical approaches for reliable detection and identification of metal soaps⁴ or constructing computational models for prediction of processes taking part during polymerization of paint films⁶ all attempt to describe this complicated degradation mechanism with the aim to find a suitable conservation, prevention and protection strategy for precious artworks.

In a number of experimental studies, model systems were considerably simplified in order to (i) examine the role of particular factors and components and/or (ii) to obtain experimental results in a reasonable amount of time since the actual processes are supposed to be long-term.^{2,6} However, since the drying of oil paints is a complex collection of individual reactions⁷ some unpredicted processes may be overlooked.

Within this study, we used natural drying oils instead of pure individual FA for mock-ups. The binary model paints were prepared by mixing minium (Pb_3O_4) with linseed, walnut, poppy-seed and standoil representing the commonly used oil binding media. One of the unexpected results was a newly crystallized lead formate, $Pb(HCOO)_2$, identified unambiguously by XRPD and confirmed also by ¹³C and ²⁰⁷Pb ssNMR.

In the past, various metal formates were observed as corrosion products on metal artifacts consisting of lead, copper or their respective alloys, but also on glass or calcareous objects.^{8–11} In case of paintings, the only reported example is the detection of zinc formate dihydrate $(Zn(HCOO)_2 \cdot 2H_2O)$.¹² It was identified together with $Zn(CH_3COO)_2 \cdot 2H_2O$ and ZnS as a degradation product of zinc white (ZnO) on the surface of Dalí's paintings Couple with Clouds in their Heads (1936). Regardless of the source of the metal cation, formic acid emitted from wooden frames, storage boxes or showcases was supposed to be the corrosion cause. However, here presented findings clearly demonstrate that drying oils alone represent another source of formic acid for the crystallization of Pb(HCOO)₂ during the formation of paint film. Lead formate has never been reported for oil-based paints, as it does not form in overly simplified systems and is probably no longer present in aged paintings or mock-ups. The role of this intermediate phase in the process is now going to be clarified.

Experimental section

Model experiments

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Model paints The model paints were prepared as binary mixtures consisting of a lead-based pigment minium (Pb₃O₄; Sigma Aldrich, p.a.) and drying oil in the weight ratio 1:3, respectively. We used the following drying oils: linseed oil (LO; Kremer Pigmente), stand oil (SO; pre-polymerized linseed oil; Kremer Pigmente), walnut oil (WO; Kremer Pigmente) and poppy-seed oil (PO; Kremer Pigmente). After thorough mixing, the mixtures were applied on a support and the freshly prepared films were analyzed immediately and then monitored regularly during their hardening (up to 2 months) without any additional treatment. For comparison, a paint prepared from the pre-reacted suspension of minium and linseed oil was analyzed. The suspension was placed into a close vial and shaken constantly on a laboratory shaker for one month. After sampling, the suspension was applied on a support as the freshly prepared paints and analyzed during drying. The samples were stored under laboratory conditions (T = 23 ± 2 °C, relative humidity (RH) was 40 %). For the XRPD measurements in a transmission mode, the paint films were prepared on the Mylar foil (polyester, 6 micrometers thick). For FTIR measurements in the reflection mode, the thin paints were applied on a laboratory glass slides covered by an aluminium foil in order to achieve the maximal reflectivity of the specimens and to avoid deformations of acquired spectra. The starting pigment was characterized by XRPD including the Rietveld refinement (Fig. S1, S2 in ESI) and the distribution of the particle size was determined by the laser diffraction analysis and the scanning electron microscopy (Fig. S3, S4 in ESI). The experimental details of this characterization are given also in ESI.

Exposure to oil vapors A thin layer of minium powder was applied on a surface of a Si zero background sample holder (Siplate). The specimen was placed on a ceramic support above the appropriate oil into a closed glass vessel, avoiding any contact between the powder and the oil similarly as reported by Ghiara et al.⁹ This setup was prepared separately for LO, PO and WO. The samples were quickly analyzed by powder XRPD every 7 days.

Synthesis of lead formate

Lead(II) formate ($Pb(HCOO)_2$) was synthesized by the reaction of basic lead(II) carbonate (($PbCO_3$)₂· $Pb(OH)_2$; Sigma-Aldrich) with formic acid (HCOOH, Lachema a.s., p.a.). The basic lead carbonate was heated with an excess of formic acid (i.e., thirty-times of stoichiometric amount) under reflux for one week. Then the reaction mixture was evaporated to one third of the

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initial volume and left to precipitate at room temperature. Solid product was filtered out, washed with isopropylalcohokandicle Online dried at 65 °C. Yield was 92,5 %. Phase purity was confirmed by X-ray powder diffraction.

X-ray powder diffraction (XRPD)

Model paints The model paints were monitored by XRPD according the following time schedule:

Time of hardening (days)	Interval of measurements
0-5	12 hours
8 – 51	7 days

Diffraction patterns of model paints were collected using a PANalytical X'Pert PRO diffractometer equipped with a conventional X-ray tube ($Cu_{K\alpha}$ 40 kV, 30 mA, line focus) in transmission mode. An elliptic focusing mirror, a divergence slit 0.5°, an anti-scatter slit 0.5° and a Soller slit of 0.02 rad were used in the primary beam. A fast linear position sensitive detector PIXcel with an anti-scatter shield and a Soller slit of 0.02 rad were used in the diffracted beam. All patterns were collected in the range of 1 to 40 deg. 2theta with the step of 0.013 deg and 200 sec/step producing a scan of about 47 minutes. The calculation of current concentration of Pb-phases in model systems based on XRPD-data is described in ESI.

Exposure to oil vapors Diffraction patterns of minium exposure to oil vapors were collected with the PANalytical X'Pert PRO diffractometer equipped with a conventional X-ray tube (Cu K_{α} radiation, 40 kV, 30 mA) and a linear position sensitive detector PIXcel with an anti-scatter shield. A programmable divergence slit set to a fixed value of 0.5 deg, incident antiscatter slit of 1 deg, Soller slit of 0.04 rad and mask of 15 mm were used in the primary beam. A programmable anti-scatter slit set to fixed value of 0.5 deg., Soller slit of 0.04 rad and Ni beta-filter were used in the diffracted beam. Data were collected in the range of 8 - 60 deg 2theta with the step of 0.0131 deg and 200s / step producing a scan of about 1 hour. XRPD data were evaluated using HighScorePlus software package (4.8.0) and JCPDS PDF-4 database.¹³

Fourier transformed infrared spectroscopy (FTIR)

The model paint film consisting of minium and linseed oil was monitored by FTIR spectroscopy according the following time schedule: every hour during the first day, then each 24 hours until the fifth day, and then once a week until the end of the first month and finally after 2 months of drying. The measurements were carried out with a Bruker Alpha II spectrometer equipped with an external reflection module which allows a fast, contactless and non-destructive FTIR analysis of large samples on top or in front of the spectrometer. Spectra were acquired in the middle infrared region (from 400 to 4000 cm⁻¹), at a resolution of 4 cm⁻¹ and by summing 32 scans. Alpha II was chosen in order to follow changes in the chemical composition during the hardening of the film avoiding any sample preparation. Qualitative evaluation of data acquired was performed with OPUS Spectroscopy Software.

Solid state NMR (ssNMR)

The ssNMR spectra were measured at 11.7 T using a Bruker AVANCE III HD 500 WB/US NMR spectrometer. The 3.2-mm and 4-mm cross-polarization magic angle spinning (CP/MAS) probes were used for ¹³C and ²⁰⁷Pb experiments at Larmor frequencies of v(¹³C) = 125.783 MHz and v(²⁰⁷Pb) = 104.609 MHz, respectively. The ¹³C ssNMR spectra were collected at 15 kHz spinning speed and ²⁰⁷Pb WURST-CPMG (Wideband Uniform Rate Smooth Truncation excitation with the Carr-Purcell Meiboom-Gill method) NMR at static conditions. The ¹³C MAR spectra of were measured with recycle delay of 20 s at the 3584 number of scans. The ¹³C CP/MAS NMR spectrum of Pb(HCOO)₂ was measured with recycle delay of 5 s. The number of scans was 256 at 1 ms spin lock. The ¹³C-¹H PILGRIM/MAS NMR spectrum¹⁴ (Phase-Inverted Lee–Goldburg Recoupling under MAS) was measured at 15 kHz spinning frequency with the number of scans 256 per increment and recycle delay of 5 s. The nutation frequency of the B₁(¹H) field for on-resonance cross-polarization and LG (Lee–Goldburg) irradiation in SEMA (Spin Exchange at the Magic Angle) recoupling sequence was $\omega_1/2\pi = 75$ kHz with resonance offset +53 kHz.

The ²⁰⁷Pb WURST-CPMG NMR experiments¹⁵ were carried out using 50 µs CT-selective WURST pulse^{16,17} using 500 kHz sweep width, with 75 loops, the recycle delay was 7 s. The applied experimental parameters were adapted from literature data.⁴ ²⁰⁷Pb WURST-CPMG NMR experiment was combined with variable offset cumulative spectroscopy (VOCS) technique.¹⁸ The final ²⁰⁷Pb WURST-CPMG NMR spectra are the sum of three sub-spectra with 178 kHz step at offsets from - 178 kHz to 178 kHz. Each sub-spectrum of model materials, Pb(HCOO)₂ and Pb₃O₄, were collected at 512 scans. In case of the prepared system (Pb₃O₄ + linseed oil) 8192 scan accumulation for each sub-spectrum were conducted. The ²⁰⁷Pb NMR spectra were referenced to the external standard Pb(NO₃)₂ (δ_{1so} = -3473.6 ppm). High-power ¹H decoupling (SPINAL64 - small phase incremental alternation with 64 steps - for MAS experiments and CW - continuous wave - for static experiments) was used to eliminate heteronuclear dipolar couplings in all measurements. The NMR experiments were

performed at a temperature of 303 K, and temperature calibration was performed to compensate for the frictional heating ticle Online of the samples.¹⁹ The all NMR spectra were processed and simulated using Top Spin 3.5 pl7 software package.

²⁰⁷Pb ssNMR signals were attributed based on spectra of the reference materials (Pb₃O₄, Pb(HCOO)₂; SI) and the obtained NMR parameters are listed in Table S1. The two signals in the ²⁰⁷Pb ssNMR spectrum of minium were assigned and fitted based on literature data.^{20,21} NMR parameters of the observed signal of Pb(HCOO)₂ was fitted based on DFT/ZORA (density functional theory with the zeroth order regular approximation) calculation²² of the structural model published by Lanza et al.²³ (CCCD deposit number 925259), computational details are listed in ESI (Table S1).

Analysis of oils and oil vapors

Determination of fatty acids in drying oils The fatty acid profiles of the drying oils used were analyzed by gas chromatography with flame ionization detector (GC-FID) according to a certified procedure in the Metrological and Testing Laboratory of University of Chemistry and Technology Prague (Testing laboratory 1316.2 accredited by the CAI according to the EN ISO/IEC 17025:2005). The determined fatty acids are given in Table S2.

GC-MS analysis of oil vapors To detect low molecular polar compounds (i.e., water and/or methanol-derivatives) the following procedure was tailored. 2 ml of each oils were placed into 4 ml vials with septum. Empty space of each vial was filled with an inert atmosphere (Argon 4.6 purity). Vials were then placed into a programmable rotator-mixer (Starlab Inc.) for a continuous mixing of 7 days. Then the samples of as formed gas over the oil were taken through the septum with gas-tight Hamilton injection syringe and immediately analyzed by a simple headspace gas chromatography (GC) method coupled with mass spectrometry (MS). Analyses were performed on gas chromatograph Agilent 6890N coupled with mass spectrometer JEOL JMS-Q1000GC. The gas chromatograph was equipped with a single injection connected with column HP-5 19091J-413 (5%-Phenyl-methylpolysiloxane, 30 m x 0.32 mm I.D. x 0.25 μ m).²⁴ Helium (purity 99.9999 %) was employed as a carrier gas. The chromatographic conditions and instrument parameters are given in Table S3.

Results and discussion

Detection of lead formate

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In the time-dependent XRPD patterns recorded on freshly prepared oil pints (Fig. 1), there is a gradual formation of two new phases. While the low angle region of the XRPD patterns has background with a broad hump which suggests the formation of lead ionomer contributing to an amorphous lead phase,³ in addition, a well crystalline phase identified unambiguously as lead formate – Pb(HCOO)₂, was formed as a secondary product in the model paints during their drying. In order to elucidate the formation of this unexpected lead phase, additional experiments and measurements were carried out.



Fig. 1 Time-dependent XRPD patterns of model paint consisting of minium and linseed (LO), poppy-seed (PO), walnut oil (WO) and standoil (SO). The XRPD patterns between 0 hours (0H) and 5 days (5D) were collected every 12 hours and, further on, every week. The detected phases: F - Iead formate, Pb(HCOO)₂, PDF 01-082-8113; M - minium - Pb₃O₄, PDF 00-041-1493; S - Pb-soap/ionomer.¹³

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¹³C ssNMR spectroscopy involving direct-polarization, cross polarization and PILGRIM experiment (Fig.2) was applied toew Article Online DOL: 10:10:39/DDDT00327A of drying and where its portion was the highest one within the studied model paints (Fig. 1). The signal assignments of ¹³C ssNMR spectra are based on literature data.²⁵ Comparing fresh and polymerized linseed oil (without pigment), significant decrease of signals corresponding to vinyl carbons from the unsaturated acyl chains (around 130 ppm) indicates terminated oxidation and evidence of broadening of all signals confirms formation of a polymeric network as expected in case of drying oils.²⁶ Furthermore, a new carbonyl signal at 177.1 ppm appearing in the ¹³C MAS NMR spectrum (Fig. 2b) suggests the presence of two distinct types of carbonyls with different local environments and mobilities in the polymerized oil network. The relative narrower signal at 177.1 ppm reflects a fraction with enhanced mobility and is attributed to carboxylic groups either corresponding to free carboxylic acids (released from triacylglycerides during polymerization of oil) and/or to carboxylic functionalities attached to the polymeric network, while the fraction reflected by a broader signal at ca. 175 ppm corresponds to ester bonds in the polymeric network. On the other hand, in the paint film with minium, the missing signal at 177.1 ppm suggests formation of lead ionomer where lead ions are bound to carboxylic groups along the polymer backbone chain.³

Additionally, experiments using the ¹³C CP/MAS NMR technique revealed two other carbonyl signals, which – based on the analysis of the ¹H-¹³C PILGRIM/MAS NMR spectrum (Fig. 2d) – are attributed to Pb(HCOO)₂. Specifically, this follows from the determined dipolar splitting which reaches to ca. 11.5 kHz. Such a high value corresponds to the one-bond ¹H-¹³C dipolar coupling constant of a rigid segment in which the distance between proton and carbon is ca. 1 Å; only formyl groups containing a carbonyl unit directly bonded to hydrogen atom (H-C=O) can be detected. Other carboxyl groups are nonprotonated therefore provide significantly smaller dipolar splitting in 2D¹H-¹³C PILGRIM/MAS NMR spectra. Consequently, detection of a large ¹H-¹³C dipolar splitting for carbonyl units identifies the presence of formyl segments (H-C=O). This assignment is further supported by the ¹³C NMR chemical shift recorded for the reference sample – lead formate (175.1 and 171.4 ppm) and by ²⁰⁷Pb NMR chemical shift (-2500 ppm) as discussed (vide infra). The two well-separated dipolar doublets resonating at 175.1 and 171.3 ppm clearly show the presence of two inequivalent formyl groups. Both these groups are quite rigid with negligible internal dynamics. The corresponding narrow ¹³C resonance and the observed large ¹H-¹³C dipolar splitting confirm a regular arrangement of both these units in one crystalline domain. The two-component character of the investigated system is further reflected by the distinctly different dipolar profiles determined for aliphatic CH₂ segments. The outer doublets with the splitting of ca. 6-7 kHz reflect relatively rigid fraction, whereas the central signal with the linewidth of ca. 3-4 kHz indicate amorphous phase with partly released segmental motions. All these findings indicate coexistence of several phases and domains including (i) a highly rigid crystalline fraction of lead formate, (ii) immobilized amorphous polymeric/ionomeric network with dissolved Pb₃O₄ and (iii) relatively mobile organic fraction, e.g., free carboxylic acids or non-crystalline soaps.

The local environment of lead atoms in the LO-based paint was investigated by ²⁰⁷Pb WURST-CPMG NMR spectroscopy (Fig. 3), which was combined with variable offset cumulative spectroscopy technique. This combination is the most suitable approach dealing with the large chemical shift anisotropy and extremely wide chemical shift range of the ²⁰⁷Pb nuclei. The obtained NMR parameters for the model paint as well as the reference Pb₃O₄ and Pb(HCOO)₂ are listed in Table 1. Signal processing and attribution is given in ESI. Apparently, lead(II) atoms (arranged in the square pyramid-coordinated PbO₄) in Pb₃O₄ react with LO preferentially during reaction to form highly crystalline Pb(HCOO)₂, while the local chemical environment of lead(IV) atoms does not change during the corrosion process, indicating that there is no redox reaction involving Pb₃O₄. The ²⁰⁷Pb NMR spectra of Pb(HCOO)₂ show chemical-shift tensors with smaller span (Ω = 720) indicating the holodirected coordination of lead atoms with 8 neighboring oxygen atoms, which was reported also for long-chain lead carboxylates (soaps) or PbCO₃.^{2,4,22}

The lead (IV) atoms probably remained in the form of nanocrystalline PbO₂ species dispersed in the polymeric matrix. This assumption could explain both, the sharp peak attributed to PbO₂ in the ssNMR spectra (Fig. 3, Table 1), indicating its crystalline nature, and on the other hand, the absent signal in XRPD patterns, indicating that the coherent domain (\approx crystallite size) remains under the detection limit of XRPD. The partial decomposition of minium accompanied by the formation of new Pb-phases (i.e., Pb-formate, Pb-soap/ionomer or PbO₂) did not lead to any observable color changes (we performed only visual inspection by naked eye) of the studied paint which remained orange-red.

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Fig. 2 The ¹³C MAS NMR spectra of a) fresh linseed oil, b) dried linseed oil, c) prepared Pb_3O_4 +linseed oil system and d) experimental 2D ¹H- ¹³C PILGRIM/MAS NMR and ¹³C CP/MAS NMR spectra of prepared Pb_3O_4 +linseed oil system. The ¹³C NMR isotropic chemical shifts were determined with the experimental error of ca. ±0.1 ppm; and the ¹H-¹³C dipolar couplings with ca. ±1 kHz. These uncertainties are negligible and cannot affect interpretation of the recorded spectra.

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Fig. 3 Experimental ²⁰⁷Pb WURST-CPMG NMR spectra (black solid line), simulations of the individual lead atoms (blue dashed lines) and their sums (red solid lines) of investigated samples.

Table 1. Experimentally measured ²⁰⁷ Pb chemical shift tensor parameters of investigated sample

Sample	Site	δ _{iso} (ppm) ^[a]	Ω (ppm) ^[b]	К	mol % (± 10 %)
Pb(HCOO) ₂	Pb ²⁺	-2567±20	720±20	0.75±0.1	100
Pb ₃ O ₄	PbO	804±20	3088±20	0.72±0.1	75
	PbO ₂	-1091±20	170±20	-0.53±0.1	25
Pb ₃ O ₄ +Linseed oil	PbO ₂	-1091±20	170±20	-0.53±0.1	20
	Pb(HCOO) ₂	-2567±20	720±20	0.75±0.1	80

^[a] The data are presented using the Maryland notation, where $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$. ^[b] The span is calculated by $\Omega \approx \delta_{11} - \delta_{33}$ ($\Omega \ge 0$) and the skew is given by $\kappa = 3(\delta_{22} - \delta_{iso})/\Omega$; (-1 $\le \kappa \le +1$).²⁷

The effect of oxygen

Monitoring of the processes in the model paints by XRPD was complemented with time-dependent FTIR measurements (Fig. 4). Comparing results from both methods, it is obvious that $Pb(HCOO)_2$ starts to crystallize in the end of autoxidation reactions. These are characterized by changes in the FTIR spectrum related to isomerization and, finally, to saturation (i.e., decrease of the signal corresponding to C=C stretch of unconjugated cis-double bonds at 3010 cm⁻¹ and 724 cm⁻¹ and simultaneous arising of signals corresponding to conjugated double bonds at 1630 cm⁻¹ and 988 cm⁻¹). Once the oxidation processes are completed, a signal of C=O stretch in lead carboxylate (1533 cm⁻¹) occurs. Its broad character is in agreement with XRPD and ssNMR, where a significant signal contribution of lead ionomer prevents the detection of $Pb(HCOO)_2$ due to signal overlap³ (see Fig. S5 in ESI). On the other hand, the crystalline $Pb(HCOO)_2$ is detected unambiguously by XRPD at the corresponding time of drying (i.e., 12-24 hours for Pb₃O₄ in LO).

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Fig. 4 Time-dependent FTIR spectra of model paint consisting of minium and LO. Highlighted bands correspond to oxidation and formation of carboxylates.

The necessity of atmospheric oxygen for formation of $Pb(HCOO)_2$ is also illustrated with XRPD patterns recorded on the paints prepared from (i) freshly mixed LO and minium and (ii) pre-reacted mixture of minium with LO (shaken in a closed vial for 1 month), Fig. 5. In both cases, the amount of $Pb(HCOO)_2$ increases with the time of drying. The minute amount of $Pb(HCOO)_2$ in the pre-reacted mixture (see XRPD pattern in Fig. 5, day 0) can be attributed to the surface oxidation of oil suspension during shaking due to the presence of air in the vial. XRPD patterns reflect also the different character of lead soap phases in both systems. In the freshly prepared paint, it is apparent that a rather Pb-ionomer phase was formed, while in the pre-reacted mixture, structural ordering with diffraction maxima in the low angles region indicate partial crystallization of lead soaps. However, detailed description of this phenomenon requires additional experimental work and is beyond the scope of this paper.

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Fig. 5 Time-dependent XRPD patterns of model paints prepared of pre-reacted mixture of minium and linseed oil, which was in form of suspension shaken for 1 month (a) and paints of freshly prepared mixture of minium and linseed oil (b). Both paints were measured by XRPD immediately after application (0D) up to two weeks during drying without any treatment or sampling. The detected crystalline phases: lead formate – $Pb(HCOO)_2$ (F), minium – Pb_3O_4 (M).

Further evidence of the oxygen effect is clearly demonstrated by the experimental exposition of minium powder to oil vapors (LO, PO and WO) without any contact of the pigment and the oil (Fig. 6). Formic acid evaporates from drying oils during their autoxidation and, reaching the minium particles, reacts to form lead formate (documented by both the increasing intensities of diffraction lines of lead formate as well as the decreasing intensities of minium). Interestingly, the time of first detectable formation of lead formate differs for the vapors of the different oils. This corresponds to the same trend found in model oil paints (Fig.1), where in the LO paint, the lead formate crystallizes promptly, while in the other oils the crystallization is slower. This indicates the effect of oil composition, which differ in the character and abundance of (poly)unsaturated fatty acids, especially in the content of α -linolenic acid with 3 isolated double bonds in the chain (Table S2).

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Fig. 6 XRPD patterns collected on minium specimens exposed to vapors of linseed (LO), walnut (WO) and poppy-seed oil (PO) for 21 days (a). The detected crystalline phases: lead formate $-Pb(HCOO)_2$ (F), minium $-Pb_3O_4$ (M). The indices denote the diffraction lines used for semi-quantitative analysis. Profiles of the relative current concentration of $Pb(HCOO)_2$ (b) and Pb_3O_4 (c) in specimens exposed to oil vapors represented by relative diffraction intensities of Pb-phases detected in the samples. The trend lines serve as a guide for eyes only.

Formic acid and the effect of unsaturation in oils

Autoxidation of drying oils is the initial step of hardening of oil films.²⁶ This involves numerous and often simultaneous reactions, representing a somewhat complicated process reflecting the complex composition of drying oils (i.e., glyceryl esters of various (poly)unsaturated and saturated fatty acids, antioxidants, etc.). In general, the reactions to be considered are the formation of unsaturated ester hydroperoxides, their decomposition and subsequent cross-linking.²⁶ The decomposition can occur via several routes, namely (i) radical recombination, (ii) radical addition and (iii) β -scission and oxidation.^{26,28} β -scission and secondary oxidation generate volatile decomposition products such as aldehydes, ketones, hydrocarbons, alcohols, carboxylic acids and other products with low molecular weight. Among the volatile organic compounds (VOCs) originating from oils, various aldehydes, typically those with 5-10 carbons, are the most abundant, while carboxylic acids belong to minor VOCs.^{7,26,28–30}

Reports on the presence of formic acids in oils containing polyunsaturated fatty acids are rather sporadic, which can reflect the fact that the analyses of edible oils focus on the detection of potentially toxic products of oxidation³⁰ or on compounds affecting the aroma, flavor or rancid odor.^{28,31,32} In addition, the choice of the method or the experimental setup can cause that some polar low weight molecules may be omitted in the analysis of the complicated mixtures of oils or their oxidation products. For example, the type of the chromatographic column as well as the temperature gradient strongly affects the possibility to detect methanol derivatives.³³

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In order to detect the formic acid in vapors of the studied oils, sample preparation and GC/MS procedure were tailored for tricle Online the qualitative analysis of methanol-related compounds and/or water in oil vapors, thus other VOCs were not detected.³⁴ Formic acid, together with formaldehyde, were detected in vapors of all investigated oils except poppy-seed oil, where no substance of interest was found (Fig. S6, S7). It is noteworthy that the formic acid predominates in the vapors of linseed oil from the bottle which was opened ca. 1 year ago, in comparison to linseed oil from a newly opened bottle (where formaldehyde was also detected), illustrating both the necessity of oxygen action and the promptness of linolenic acid to be oxidized leading to the production of formic acid.

Formic acid as a by-product of oxidation of unsaturated aldehydes, which were produced by decomposition of primary unsaturated ester hydroperoxides by autoxidation of oil triacylglycerides, is reported, e.g., by E.N. Frankel, who studied the volatile lipid oxidation products related to edible oils.²⁸ In addition, lower aldehydes formed from a cascade of oxidation reactions can be further oxidized, thus resulting in the corresponding carboxylic acid, as reported by H. Wexler.²⁶ This reaction mechanism is illustrated by the scheme in Fig. S8 in ESI. In addition, Wexler described a pathway based on the decomposition of intermediate ozonides during the polymerization of drying oils. Although unassigned, a signal was also reported at 8.27 ppm in the ¹H NMR spectra of linseed oil after 3 days of oxidation³⁰ attributable to C=O bond in formic acid.³⁵

Our results indicate (Fig. 1, 5, 6) that the rate of oxidation reactions resulting in the final formation of lead formate is different for different oils. Comparing the relative integral intensities of the most intense XRPD line of Pb(HCOO)₂ positioned at 16.9° 2 θ Cu K α , it is obvious that LO is prone to form Pb(HCOO)₂ more readily than other investigated oils in mixtures with Pb₃O₄ (Fig. 7).



Fig. 7 Comparison of the profiles of the relative current concentration of $Pb(HCOO)_2$ (a), Pb_3O_4 (b) and Pb-soap phase (c) in model paints represented by relative diffraction intensities of Pb-phases in the mixtures. The trend lines serve as a guide for eyes only.

LO consists predominantly of α -linolenic acid (C18:3n3), while the main fatty acid in both WO and PO is the linoleic one (C18:2n6c) and pre-polymerized SO contains mainly oleic acid (C18:1n9c) (Table S2). In the traditional oxidation mechanism,

the rate-limiting step in the reaction is abstraction of the hydrogen atom occurring at the bis-allylic positions (CH=CH-<u>CH2</u>Article Online CH=CH) of polyunsaturated acids (PUFA), implying that the susceptibility of PUFA to oxidation depends on the availability of the bis-allylic hydrogens.³⁶ In other words, the oxidizability of PUFA is proportional to the number of bis-allylic positions in molecules and their position.^{26,30,37,38} Therefore, three isolated double bonds as well as their position near the methyl end in α -linolenic acid affect both the rapid oxidation²⁹ and the formation of formic acid via decomposition of secondary oxidation products of the oil, resulting in rapid crystallization of Pb(HCOO)₂ in the LO-based-paint. Guillén and Ruíz, who studied the oxidation of unsaturated oils by proton NMR, concluded that the oxidation and polymerization of the linseed oil was quick due to both the rapid appearance of hydroperoxides and their rapid subsequent degradation.³⁰ The course of Pb(HCOO)₂ crystallization in WO and PO paints shows a similar trend, reflecting the close composition of Pb(HCOO)₂, however, the antagonistic effect of a relatively higher antioxidant activity of the oil^{36,39} probably reduces the amount of the evolved formic acid.

Lead formate as an intermediate

Raychaudhuri et al.⁴⁰ identified lead formates together with lead carbonates as corrosion products of lead under action of formic acid. Thermodynamic calculations indicated that lead carbonates are the final products of the conversion of lead formates depending on the variations of partial pressure of CO₂ and formic acid in the environment. It implies the probable role of lead formate as an intermediate of the binder-induced conversion of minium to lead carbonate in here-presented experiments. In the analysis of micro-samples from actual paintings, it is not easy to differentiate the primarily applied lead carbonates (i.e., lead white consisting of PbCO₃ and 2PbCO₃·Pb(OH)₂) from the secondary ones. In some cases, particle size and morphology may be indicative – lead carbonates found in the core of neo-formed aggregates were explained as products of mineralization of lead soaps.^{5,6} On the other hand, if the grains are randomly distributed in the paint layer, no definitive answer can be given.

Changes in relative concentrations of Pb_3O_4 and neo-formed lead phases in time are illustrated by plotting the relative integral intensities of their most intense diffraction lines or, in case of Pb-soaps, humps (Fig. 7). Apparently, the most pronounced consumption of Pb_3O_4 occurs in the PO paint. In the PO and the WO paint as well, the amount of $Pb(HCOO)_2$ decreases in time, indicating its partial transformation probably to an ionomer and/or nascent non-crystalline lead soap phase, which is indicated by the gradually increasing hump in the 1-10°20 Cu K α interval in the XRPD patterns (Fig. 1). While the relative amount of soaps in model paints is proportional to the content of SFA in the studied non-polymerized oils (Table S2), the variations of the Pb(HCOO)₂ content indicate its conversion to lead soaps in PO and WO systems in the investigated time horizon since no other lead-based phase was identified in the model paints.

The assumption that $Pb(HCOO)_2$ plays a role as an intermediate either for lead carbonates or lead soaps could explain its absence in paint layers obtained from artworks. However, it is necessary to admit that such substance can be easily omitted in the routine analyses of complicated paint mixtures. Therefore, an extended research of lead formate crystallization in paint systems should (i) shed light on its role and fate in oil paints in the long-term scale, (ii) examine the effect of environmental factors on its stability and (iii) evaluate how other lead-based pigments are prone to $Pb(HCOO)_2$ crystallization.

Conclusion

Lead formate was identified unambiguously by powder XRPD as a secondary product of the interaction between minium pigment and four different drying oils during the curing of the model paints.

The ¹³C CP/MAS NMR and the ¹H-¹³C PILGRIM/MAS NMR techniques revealed the co-existence of crystalline lead formate within the immobilized amorphous polymeric/ionomeric network with dissolved Pb_3O_4 and relatively mobile organic fraction.

²⁰⁷Pb WURST-CPMG NMR spectroscopy combined with variable offset cumulative spectroscopy technique was applied to investigate the local environment of lead atoms in the LO-based paint, providing the NMR parameters for Pb_3O_4 and $Pb(HCOO)_2$ and showing that lead(II) atoms in Pb_3O_4 react with LO preferentially during reaction to form highly crystalline $Pb(HCOO)_2$, while lead(IV), having the unchanged chemical environment, is not reduced to Pb(II).

The evaporation experiments and the GC/MS procedure of oil vapors tailored for the detection of polar low molecular volatile compounds proved the emission of formic acid from the drying oils during their autoxidation.

The different rate of the formation of lead formate in the drying oils depends on the number and position of double bond in the fatty acid chains, i.e., on the availability of bis-allylic hydrogen for the hydrogen abstraction representing the rate-limiting step of the oxidation of oils.

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Lead formate is assumed to be an intermediate product contributing either to the formation of lead carbonates and/orecoArticle Online DQI: 10.1039/DODT00327A lead soaps. It is important to realize that the rapid formation of lead formate during the initial stages of paint drying might be a source for further degradation of paint layers induced by a conservation treatment. Thus an incorporation of monitoring of the chemical changes during the treatment would be beneficial to control the process.

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Lead formate was found in the oil paint system, crystallizing in the early stage of polymerization of oil paint and playing role as an intermediate in the degradation of lead pigment.

