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# Lead soaps in paintings: friends or foes?

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## **Abstract**

The origin(s) and role(s) of metal soaps in paints are a worldwide concern today. These hybrid compounds, containing both fatty organic chains and metals associated thanks to a carboxylate function, are increasingly identified in paints. As reviewed in the first part of this work, the presence of metal soaps in paints is differently interpreted in scientific publications: metal soaps are sometimes considered to play a positive role as anchor points, during the paint drying processes; they can also be considered as responsible for many degradation processes (protrusions, efflorescences, darkening, etc.). Their origins are also interpreted in various ways. In some paintings (in particular from the 20<sup>th</sup> C.), they were sometimes introduced on purpose, as such, as additives, to master the physical properties of the painting materials. In older paintings, metal soaps are usually thought to result from an uncontrolled reaction of oil with lead pigments, in particular lead white, red lead and lead tin yellow, mainly. In the second part of this work, the review of historical recipes of lead media shows an important number of recipes based on the controlled mixture of oil with lead driers. In the third part, the experimental reproduction of such traditional recipes using walnut oil and litharge (PbO) shows that lead soaps can be formed, both in ~1h at ~100°C, or in ~1 month at room temperature. It shows as well that after a few years, litharge is no longer detected in the paint medium, while different lead carbonates are. Finally, the micro-infrared spectroscopy and micro-X-ray diffraction re-analysis of protrusions from a 9-year model painting shows together with lead soaps, the presence of  $Pb_5(CO_3)_3(OH)_2O$  ("synthetic plumbonacrite"), an unusual phase recently observed in a protrusion from a painting by Vincent Van Gogh. This work highlights i) the multiple origins and roles of metal soaps in paints and ii) the importance to combine the analysis of fragments from historical paintings with the analysis and reproduction of historical recipes. In particular, we show that the components detected today in historical paintings may severely differ from those originally used or prepared by the painter, complicating the assessment of the painter's intentions. More than the presence of metal soaps, the key questions to be tackled should be about their origins and (re)mobilization.

**Keywords:** Metal soaps; Metal carboxylates; Lead driers; Lead soaps; Paints; Paintings; Litharge; Protrusions;  $\mu$ FTIR;  $\mu$ XRD; synchrotron micro-analyses

## Study of metal soaps in paintings: A worldwide concern of high relevance

### [Heading]

Metal carboxylates have the general formula  $M(\text{RCOO})_n$ , with M a metal and R an organic group. When R is a fatty chain, these compounds are named “metal soaps”. The earliest report of the use of metallic soaps (obtained by combination of lime (CaO) with fats) is as waterproof lubricants in the wheels of 1400 B.C. Egyptian wheel bearings (Corkery, 1998). In paints, metal soaps usually result from the reaction of a metal base with an ester or acid group, from oil triglycerides. However, few publications also report the formation of metal soaps from reaction with beeswax (Liang & Scott, 2014) or egg yolk as well (Salvadó, *et al.*, 2009). The presence of metal soaps, in particular lead soaps, in master paintings is today probably one of the most, if not the most, recurrent topic in the worldwide research programs related to chemical analysis of paintings. Several dedicated research works have been or are carried out on this specific subject in major centers of research for art and archaeology. Historically, the pioneer studies were initiated by the FOM institute AMOLF group (Van Den Berg, *et al.*, 1999) and, among others, the Netherland Institute for Cultural Heritage in Amsterdam, the Royal Cabinet of Paintings Mauritshuis in The Hague (Noble, *et al.*, 2000), as well as many other institutes through the so-called “MOLART” (Molecular Aspects of Ageing in Painted Works of Art) project (Clarke & Boon, 2003). At the same time, similar attention was drawn to metal carboxylates detected in 35 paintings from the 13<sup>th</sup> to the 18<sup>th</sup> Century, at the National Gallery (Higgitt, *et al.*, 2003). With these two groups, studies were focusing on so-called “protrusions”, sorts of globules usually white or orange, breaking the painting surface (see an example in Fig. 4C). These two research groups demonstrated that these protrusions were made of lead fatty carboxylates. Most often, and even if the protrusions are detected as superficial holes in the surface of the painting, they originate from the internal “preparation layer(s)”: coating layers applied on the substrates, being wall, wood, canvas, etc, to provide a uniform and flat surface for painting. Less often protrusions are formed in upper paint layers (Boon, *et al.*, 2002), suggesting that the specific composition of ground layers may have a fundamental role in the formation of protrusions. At the same period, at the Canadian Conservation Institute, both the review of 19<sup>th</sup> C. recipes of lead-based media and the synthesis of reference metallic soaps were carried out (Carlyle, 1999, Corbeil & Robinet, 2002). In France, metallic soaps were also studied at the Center for Research and Restoration of French Museums, Louvre, but through the analysis of antic lead based cosmetics and of ancient pharmaceutical recipes for lead plasters (Cotte, *et al.*, 2005).

Today, the presence of metallic soaps in paintings raises chief attention in major research centers associated to museums. Among others, let's refer to the National Gallery (<http://www.nationalgallery.org.uk/paintings/research/meaning-of-making/vermeer-and-technique/formation-of-lead-and-zinc-soaps>), the Metropolitan Museum (<http://www.metmuseum.org/research/conservation-and-scientific-research/lead-soaps>), the Centre for Contemporary Art Conservation, South Brisbane (Osmond, 2014). Interactions between lead and zinc white and organic material is the subject of a European project (LeadART) associating 10 major

European art and archaeology research centres (<http://www.heritageportal.eu/Browse-Topics/PAINTINGS-PAINTED-SURFACES/Induced-decay-and-ageing-mechanisms-in-paintings-Focus-on-interactions-between-lead-and-zinc-white-and-organic-material.html>). It is a central aspect of the PAinT (Paint Alterations in Time) project led by the University of Amsterdam and many Dutch museums such as the Rijksmuseum and the Van Gogh museum (<http://www.s4a-paint.uva.nl/>). A dedicated conference “Metal Soaps in Art” has been organized in March 2016 (<https://www.rijksmuseum.nl/nl/nu-in-het-museum/symposia/metal-soaps-in-art>). In a few words, “metallic soaps” are receiving today an international attention.

A major initiative which had a tremendous impact on this research was the questionnaire sent to conservators and conservation departments of museums worldwide by P. Noble and J. Boon in 2002 in order to review the occurrence of “metal soap formation in oil paintings”. The objective was more particularly to report a set of degradation phenomena for which metal soaps were suspected to play a major role. Part of the results was published in 2005 (Noble, *et al.*, 2005). This review showed that metal soaps have been found in thousands of paintings, lead and zinc soaps being the most commonly found. Copper soaps are rarer and linked to green glazes. Few cases of potassium and calcium soaps have been reported as well (Boon, private communication). In addition to the “protrusion” phenomena, metal soaps were found to be associated with many other degradation phenomena: for example, efflorescences (Ordonez & Twilley, 1997), darkening due to increased transparency (Noble, *et al.*, 2005), delamination (Helou-de La Grandiere, *et al.*, 2008) exudates and drips (Boon & Hoogland, 2014), cracks (Duffy, *et al.*, 2014), among others. Most of nowadays studies highlight degradation phenomena associated to the presence of metal soaps in the world of cultural heritage.

Today, metal soaps are essential ingredients of various industries: mainly in paintings (in particular coating vehicles) as driers and anti-settling, wetting, matting, dispersive agents, but also as antifoaming agents in aircraft lubricating oils, detergents in dry cleaning, fungicide treatment of wood, waterproofing agents on fabric, paper, masonry, and metals, heat, light stabilizers in plastics, (Corbeil & Robinet, 2002, Kastens & Hansen, 1949). “*With the advent of modern, finely divided pigments, especially the organic pigments, fatty acid salts were added to compensate for the loss of wetting ability*” (Ordonez & Twilley, 1997). As an example, in 1920, aluminium and zinc stearates were patented for helping grinding pigments and preventing settling or separation of pigment from media (Tumosa, 2001). The use of metal soaps is also now extended to many fields of materials sciences, where they can be used as precursors of nano-films, nano-composites, nano-particles, in homogeneous catalysis as well (Mishra, *et al.*, 2007), chemical thickeners in greases, anticaking agents for powdered substances, solid lubricants for drawing wire or metal tubing, among other uses (Corkery, 1998). Extensive studies have explored alternatives to lead (for example zinc, manganese, copper, calcium, cobalt, aluminum or zirconium), and to (un)saturated linear fatty chains (for example tallates, naphthenates, octoates) (Corkery, 1998, Kastens & Hansen, 1949, Soucek, *et al.*, 2012). Metal soaps are now extensively found in modern paintings and this is usually associated with the intentional (even if not perfectly controlled) introduction of these materials in the paint either by the paint supplier and/or by the artist (Van den Berg, 2016). However, as detailed below, while they were introduced for good reasons, it turns out that they can also be responsible for various degradations.

Consequently, behind the simple question “are metal soaps (systematically) associated to degradation?”, there are more complex questions such as: i) “do metal soaps result (systematically) from degradation?” and ii) “are metal soaps systematically responsible for degradation phenomena

and/or, can they have positive effects on paintings?”. Said differently, it is fundamental to determine both the origin(s) and the role(s) of metal soaps in paints.

After a review of analytical techniques available for detection (and possibly localization) of metal soaps in paint cross-sections, we review scientific publications reporting the detection of metal soaps in historical paints. In particular, we discuss how the presence of metal soaps is interpreted (with positive, negative or neutral terms). In the specific case of lead soaps, we review the different lead compounds (lead pigments and/or lead driers) possibly responsible for the formation of lead soaps in historical paintings, and how this evolves across centuries. In a second part, we review historical recipes of lead-oil media, and we show how these recipes evolved from Antiquity to modern times, in terms of ingredients and procedure. In the last part, we present experimental reproductions of some of these recipes and show how fast lead soaps can be formed following these recipes. We also study the long term behavior of such systems by re-analyzing a 9-year old model paint, exhibiting lead soaps protrusions. With this multi-angle approach, we aim at showing the complexity and the many possible answers to the question: “metal soaps in paintings: friends or foes?”.

### Identification of metal soaps in paintings: a dramatic evolution of the analytical techniques [Heading]

One reason for this sudden universal occurrence of metal soaps in paintings is probably more due to their specific inspection, than to a rapid popping-up on paintings. This is related to the evolution in analytical techniques available for the identification of the chemical composition of paintings. Using conventional techniques, the detection and localization of metal carboxylates in paint cross-sections is difficult (Van der Weerd, *et al.*, 2002). Historically, in combination with visible microscopy (aided by specific staining), the main techniques used for identification of painting ingredients are Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS) and gas chromatography coupled with mass spectrometry (GCMS). The former gives access primarily to elemental identification of pigments and inorganic additives and the latter to the molecular identification of organic binders and varnishes. GCMS in particular offered a major tool for following chemical changes during oil drying (Mills, 1966). In their standard use, however, these techniques are not appropriate for the detection of metal carboxylates, hybrid compounds made of a (usually heavy) metal with an (organic) fatty chain, bonded through carboxylate functions. SEM-EDS detects carbon, oxygen and the metal, but these different elements can also be present in carbonates and their elemental co-location is not enough to deduce a molecular composition. Carboxylates can only be hypothesized but not proven based on a different grey level in BSE images (Keune, *et al.*, 2011). As an example, SEM-EDS was used to study darkening of paintings as a result of increased transparency (Noble, *et al.*, 2005). The SEM-BSE comparison of the *imprimatura* layer in cross-sections from both non-darkened and darkened area of the sky displayed in a panel painting by Aert van der Neer dated mid-1650s, *River Landscape* (Mauritshuis inv. no. 912), show striking differences. In the undarkened area, lead white particles are both fine and coarse and homogeneously distributed. Conversely, in the darkened area, only large coarse lead white particles are present. In addition, other particles appearing as grey halos in the SEM-BSE images (lower density of lead) suggest that lead white progressively transformed into lead soaps, increasing the transparency, in particular of the *imprimatura* layer (Noble, *et al.*, 2008, Noble, *et al.*, 2005). In *Dancing Peasants at an Inn*, by Jan

Steen (c. 1644-48), a similar darkening was observed as the result of saponification of lead white in paint layer (grey-blue sky layer) (Noble, *et al.*, 2008).

For GCMS, the traditional sample preparation requires hydrolysis and methylation of the fatty carboxylic groups, reacting indistinctively on esters, free acids and metal carboxylates (Schilling & Khanjian, 1996). Indeed, GC was used in the 1970s together with staining tests for the pioneer attempts to identify the nature of inclusions in old-master paintings and wrongly led to the conclusion that inclusions were due to the use of a binder made as an emulsion of egg (an aqueous medium) in oil (a non-aqueous medium) (Higgitt & Plater, 2004, Spring & Higgitt, 2006).

Conversely to SEM-EDS and GCMS, Fourier Transform Infrared (FTIR) Spectroscopy is a close-to ideal technique for probing complex mixtures of organic, inorganic and hybrid ingredients (Casadio & Toniolo, 2001, Meilunas, *et al.*, 1990, van der Weerd, *et al.*, 2004). FTIR instruments are rather cheap, easy to use and can even be employed on site with portable equipments. The sample does not require complex preparation –if any as in GCMS and is not affected by the analysis allowing further studies. Accordingly, this technique is commonly used for the identification of painting composition. In the particular case of metal soaps in paints, the metal associated to the carboxylate group can be identified thanks to characteristic CO asymmetric ( $\nu_{as}(\text{CO})$ ) and symmetric ( $\nu_s(\text{CO})$ ) stretching peaks (Otero, *et al.*, 2014, Robinet & Corbeil-a2, 2003). As an example, Salvado *et al.* could identify and differentiate lead, calcium and copper carboxylates in fragments from 15<sup>th</sup> C. paintings and model paintings, thanks to  $\nu_{as}(\text{CO})$  peaks as a doublet at 1540 and 1513, a doublet at 1576 and 1539, and a singulet at 1585  $\text{cm}^{-1}$ , respectively (Salvadó, *et al.*, 2009). If the organic chains are sufficiently well organized (in particular in the case of fully saturated chains such as stearic or palmitic chains), a characteristic series of small peaks assigned to wagging and twisting-rocking vibrations of methylene groups from the fatty acid chains even permits the determination of the length of the chains. This is relatively straightforward on pure crystallized references (Robinet & Corbeil-a2, 2003) but has also been possible on fragments of protrusions from historical paintings (Cotte, *et al.*, 2007, Higgitt, *et al.*, 2003). Fatty chains in metal soaps can also be identified with Raman spectroscopy (Otero, *et al.*, 2014).

The introduction of FTIR microscopy, being in reflection mode (Heeren, *et al.*, 1999, Van der Weerd, *et al.*, 2002), in Attenuated Total Reflectance mode (Spring, *et al.*, 2008), optionally using synchrotron-radiation (SR) beam (Cotte, *et al.*, 2009, Salvado, *et al.*, 2005) opened the way for chemical mappings and is nowadays a standard technique for the chemical imaging of painting cross-sections. Indeed, in the present context, localization of metal soap is as important as identification. The specific localization of compounds in non-degraded or degraded areas will be an important clue to determine if these compounds are involved in degradation (possibly as reactants and/or as products of degradation). As an example, specific concentration of metal soaps in protrusions or efflorescences supports their role in the degradation process (Boon, *et al.*, 2002). In the darkened “River landscape” quoted above,  $\mu\text{FTIR}$  was also used confirming metal soap formation in the transparent regions of the *imprimatura* layer (Noble, *et al.*, 2005). These different examples show that it is highly valuable to access the localisation of the different compounds, and, in the case of degradations, to analyse both safe and degraded areas. In this respect, all microscopy techniques are highly valuable. Similarly to  $\mu\text{FTIR}$ , Static Secondary Ion Mass Spectrometry (SIMS) has been successfully used for identification and localization of metal soaps in painting cross-sections, giving even more detailed identification of molecular composition of the fatty acid (Heeren, *et al.*, 1999).  $\mu\text{FTIR}$  and SIMS are now regularly used, alone or together, to detect the possible presence of metallic carboxylates in painting cross-sections.

Recently, Zumbühl et al. proposed a derivatization technique to increase spectral selectivity of  $\mu$ FTIR (Zumbühl, *et al.*, 2014). When FTIR spectra present a strong signal from metal carboxylates and/ or carbonates, derivatization using gaseous  $\text{SF}_4$  allows controlled elimination of these bands. This derivatization procedure has been successfully exploited previously with  $\text{SF}_4$  and  $\text{NO}$  to quantify oxidation products such as carboxylic acids, ketones and alcohols, formed during the curing of linseed oil with cobalt drier (Mallégol, *et al.*, 2000). It could be interesting to apply similar derivatization procedures, in order to map first (before derivatization) all components, in particular carboxylates and carbonates, and re-analyze samples after derivatization, to get a better sensitivity and identification of other molecular groups from the binders (e.g. oxidation products such as alcohols, carboxylic acids; small proteins contents, resinous components). This would allow a more sensitive and specific detection and localization of the different compounds involved in the curing of “oil-pigment” and “oil-drier” model systems.

Similarly, the use of fully deuterated fatty chains, as alternative to fully hydrogenated fatty chains should be considered to provide additional contrasts in  $\mu$ FTIR and SIMS chemical mapping. This has already been exploited to follow transdermal diffusion of lead soaps and fatty acids in skin, as a first step to estimate the toxicity of lead soap-based cosmetics and pharmaceutical products used since Antiquity (Cotte, *et al.*, 2004). This chemical contrast (the symmetric stretching peak  $\nu_s(\text{CD}_2)$  is shifted down to  $\sim 2088\text{cm}^{-1}$ , compared to  $\sim 2850$  for  $\nu_s(\text{CH}_2)$ ) could be similarly exploited to specifically map some compounds (e.g. fatty acids, or fatty soaps) in a complex paint model system and follow their short term and long term diffusion, aggregation, crystallization, etc...

At a completely different scale (full painting scale), a macroscopic FTIR scanning instrument has been recently proposed which permitted full imaging of a 19<sup>th</sup> C. Russian house icon depicting Saint Nicholas of Myra (wooden panel,  $14 \times 18 \text{ cm}^2$ ), visualizing the distribution of Zn carboxylates and allowing comparison with the Zn elemental distribution obtained by macro-X-Ray Fluorescence (XRF) (Legrand, *et al.*, 2014). Such technique combinations offer unique identification and localization of the chemical environment of Zn and is very promising for future 2D mapping of metal soaps at paintings scale (Legrand, *et al.*, 2014).

In addition to spectroscopic techniques, X-ray diffraction (XRD) has also been identified as an efficient non-destructive characterization method of metal carboxylates. In 1941, Jacobsen reported the identification of zinc soap in linseed oil paints containing zinc oxide (Jacobsen & Gardner, 1941). The few references available in the International Center for Diffraction Data (ICDD) motivated the synthesis and characterization of some key metal carboxylates (Corbeil & Robinet, 2002). Similarly to FTIR, the extension to microscopy was made possible thanks to synchrotron sources, allowing the identification and precise localization of carboxylates (as well as inorganic ingredients such as pigments and degradation productions) in cross-sections of tiny historical and model paint fragments (Cotte, *et al.*, 2008, Salvadó, *et al.*, 2009).

Besides fully exploiting 2D imaging techniques, a few studies recently explored the third dimension and obtained a full 3D description of soap protrusions (morphology, elemental composition, crystalline phase composition) using state-of-the-art SR based micro-analytical techniques, namely SR micro-tomography (Ferreira, *et al.*, 2009), SR confocal  $\mu$ XRF (Faubel, *et al.*, 2011) as well as SR 3D  $\mu$ XRD (Vanmeert, *et al.*, 2015), respectively.

In addition to these imaging techniques, other methods, many of them macromolecular probes, were also used and developed to probe the presence and nature of metal carboxylates in paintings: for example, thermogravimetric analysis (Bonaduce, *et al.*, 2012), Nuclear Magnetic Resonance (Catalano, *et al.*, 2014, Verhoeven, *et al.*, 2006), potentiometry, electrical conductivity, turbidity

(Pereira, *et al.*, 2014) and direct temperature-resolved time-of-flight mass spectrometry (van Loon, *et al.*, 2016). Even if such techniques are destructive and cannot always be applied to precious historical samples, they are of interest to understand reaction processes on model paints. A comparison of pros and cons of many analytical techniques applied to the study of interactions between the Naples yellow (lead antimonate) pigment and oil (in particular the detection of metal carboxylates) can be found here (Keune, *et al.*, 2009). Beyond the scope of paintings, Corkery gives a very detailed review of uses, identifications and characterizations of metal soaps, through History (Corkery, 1998).

Thanks to all these methods, metal soaps can be detected and studied more and more efficiently and accurately in historical and model paintings, as illustrated by the increasing number of reports in scientific publications (Fig. 1). This set of references (scientific publications mentioning “metal/lead soap/carboxylate” and “paint\*”, as referenced under SCOPUS) may not be exhaustive, but is sufficiently large to show how this research topic has evolved over the last 15 years (Table S1).

## Review of the scientific publications reporting the detection of metal soaps in historical and model paintings [Heading]

### Terminology used to describe metal soaps in paintings [Subheading]

In Fig. 1, 143 scientific publications have been sorted in four categories, depending on the suspected origin(s) and/or role(s) of metal soaps in paintings. Typically:

- for “negative” class, publications reporting metal soaps associated to the different degradations listed in the introduction (e.g. protrusions, efflorescences, darkening due to increased transparency, exudates and drips), and/or describing metal soaps as “degradation products” without further detailing any macroscopic degradation.
- for “positive” class: publications reporting positive roles associated to metal soaps, e.g. used as driers, dispersive agents, antifoaming agents, detergents, fungicide, waterproofing agents, etc, in particular in modern paints. Besides, other publications detail the positive role of metal soaps for the stabilization of polymer network (see details below).
- The class “both” means that both positive and negative roles are mentioned in the same publication, not necessarily for the same painting.
- The class “neutral” refers to the publications where metal soaps are not associated to any particular controlled synthesis nor use, and they are not associated to any degradation neither. Metal soaps are usually described as “reaction products” or “conversion products” without any interpretation of the possible negative or positive impacts of these reactions.

While today metal soaps are usually perceived mainly as pernicious compounds (in 2015, 80% of the publications were reporting “negative” metal soaps (60% “negative” and 20% “both”), the terminology used to refer to their role in paints evolved over the last 15 years.

In the early detections of metal soaps (in particular lead carboxylates) in painting cross-sections, metal soaps were considered as major positive actors of the so-called “**maturation processes**” when they were detected homogeneously and not specifically in protrusions (Van Den Berg, *et al.*, 1999). The authors proposed that “*metal ions at the surface of pigment particles as well as dissolved ions (from pigments or driers) can act as **anchor points** for the carboxylic acid groups. Multivalent interactions lead to complex linkages between different parts of the polymer network. [...] It is known (Holliday 1975) that metal carboxylate formation in polymers (to ionomers) leads to a large increase in hardness and stiffness of the paint film. As a result of the increased compactness by electrostatic*



forces, the swelling probability is strongly decreased and the paint becomes somewhat brittle. Without **stabilisation** of the hydrolysed/paint by metal ions, the paint film will be more vulnerable to swelling. In this case liberated [fatty acids] can appear at the surface (blooming), evaporate (precipitation on the protective glass) or become extracted”.

Conversely, the word “degradation” is associated to the transformation of “the triglyceride radicals into low molecular weight (un)saturated aldehydes, ketones, alcohols, acids, and hydrocarbons responsible for the typical smell of drying oil paints. Most of these smaller volatile molecules arise from the hydrocarbon chain of highly unsaturated fatty acid moieties and will generally leave the paint film by evaporation, although short chain FAs may be trapped within the paint film for a longer period of time.” (Van Den Berg, et al., 1999).

Interestingly, such “degradation” can affect the metal carboxylates themselves: “metal carboxylates already present [may be affected by photochemical degradation leading to small breakdown products and loss of organic materials] and the paint may lose its binding capacity leading to an increased extractability of organic fractions”.

Similarly, in a pioneer SIMS analysis of a cross-section of a fragment taken from an Early Netherlandish painting by Rogier van der Weyden, Keune et al. observed an almost homogeneous distribution of lead carboxylates in the three upper blue layers of the stratigraphy. “Fatty acids and fatty acid soaps show highest ion yields near lead white, a mineral pigment that serves as a natural chemical drier and is proposed to act as a **template for the initial grafting** of the polyunsaturated triglycerides of the linseed oil. [...]The fatty acid lead soaps point toward a **mature** ionomeric oil paint system that developed over centuries.” (Keune & Boon, 2004)

In a study comparing model paintings prepared from lead white in freshly pressed linseed oil, naturally aged for 3 years and artificially aged, it appears that “the artificially aged approached compared with the natural aged a mature oil paint, owing to the presence of metal soaps and **absence of degradation products** [=small chain fatty acids, diacids]”. (Keune, et al., 2005)

In another work, lead carboxylates were also said to positively act in a “**self-repair mechanism** in which [they] bind these loose ends with limited volume change into a metal coordinated network” (Boon, et al., 2006).

Conversely, today the presence of metal soaps tends to be quasi-systematically associated to degradation. As an example: “The formation of metal soaps is a major problem for oil paintings conservators. The complexes of either lead or zinc and fatty acids are the product of reactions between common pigments and the oil binder, and they are associated with many types of **degradation** that **affect** the appearance and stability of oil paint layers.” (Hermans, et al., 2015)

A few publications are more neutral, referring to “aging”, “conversion”, “reaction”, or “alteration” as well. Here it should be noted that the connotation of the word “alter” differs from one Latin-based language to another. While the French “altérer”, the Italian “Alterare”, the Spanish “Alterar” would translate into to distort, to spoil, to impair, to affect, to disturb, to corrupt and has today a quasi systematic negative sense, the English “to alter” means to change, to modify, but without any negative or positive connotation. Hence the sentence by C. S. Tumosa and M. F. Mecklenburg (Tumosa & Mecklenburg, 2005): “Lead compounds or pigments alter the drying behavior and physical properties of oil paints and varnishes, enabling artists and craftsmen to tailor the properties most suited for their purposes.”

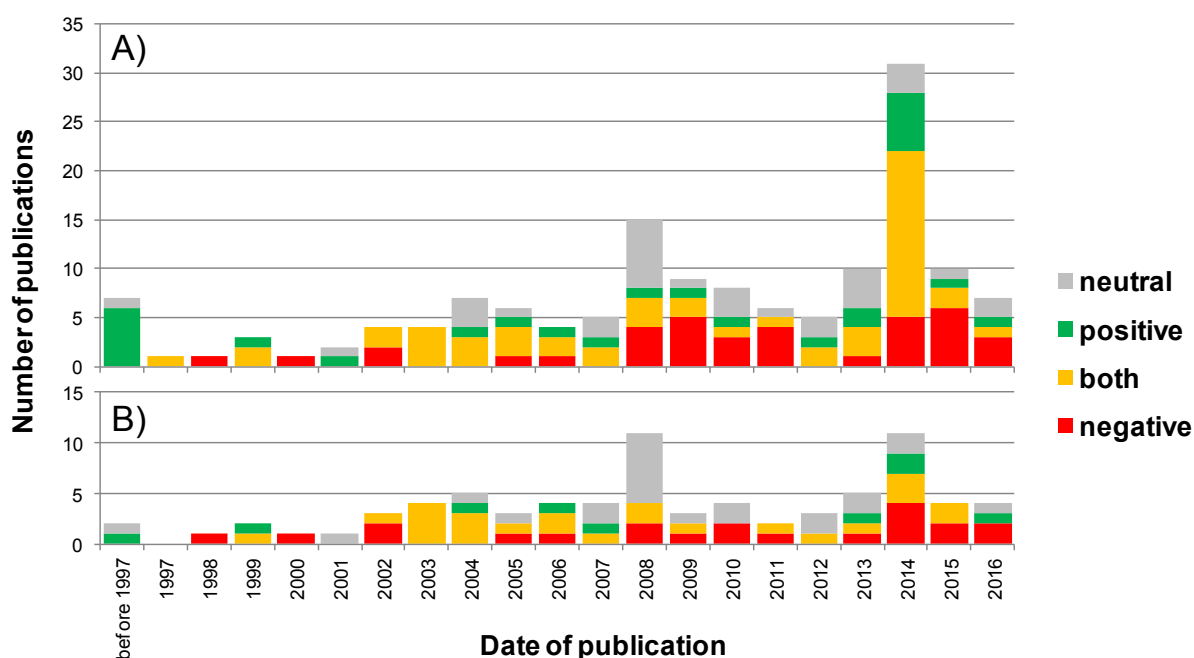


Figure 1: Evolution of the number of scientific publications reporting the putative origins and roles of metal soaps in paintings. Publications are sorted into four categories referring to the possible impacts of soaps as interpreted by the authors: negative, positive, both (both mentions of positive and negative impacts in the same publication) and neutral, depending on the origin(s) and role(s) associated with the metal soaps (see text for details). A) shows a review over 148 publications (paintings from all periods), B) excludes publications which mention “modern” (>1850) paintings. List of publications given in Table S1.

Fig. 1A and 1B differ by the fact that in Fig. 1B, all the publications mentioning the analysis of a “modern” (dated after 1850) painting are excluded, while Fig. 1A shows the full set of publications. These figures show: i) the rather high proportion of detection of metal soaps in “modern” paintings (almost half of the publications), ii) the fact that positive effects of metal soaps are more often mentioned for paintings of this period (in “modern”: 24% “positive” and 38% “both”, vs. 11% “positive” and 30% “both” for paintings earlier than 1850), iii) related to that, a high proportion of “both”, meaning that these metal soaps, introduced for good reasons can also be responsible for degradation. As an example, among the 27 works recently published in the book “Issues in Contemporary Oil Paint”, 12 mention the presence of metal soaps, playing a role in deterioration phenomena. iv) for paintings dated before 1850, the presence of metal soaps is more often qualified as “neutral”, meaning associated to a naturally aging of paint, and not to a volunteer action of the painter (27%, vs. 13 % for “modern” paintings).

When metal soaps, in particular lead soaps are not introduced as such in paints (as in 20<sup>th</sup> C. paints), they usually result from the reaction of a metal compound with an ester or acid (e.g. oil). It is therefore very important to characterize the inorganic phases associated with metal soaps, because this can give clues about the origins of metal soaps. The following paragraph discusses this aspect in the particular case of lead soaps. Similarly to lead soaps, the same question: “are these lead inorganic compounds original ingredients or formed with time” should be tackled carefully as well.

The different inorganic lead compounds detected or hypothesized in association with lead soaps  
[Subheading]

The forms under which lead could be incorporated into oil paint are many and evolved with time (Carlyle, 1999, Tumosa & Mecklenburg, 2005). They have two main functions: pigments and/or driers. The same compound (in particular lead white and red lead) can be used for both purposes. Fig. 2 shows the forms of lead which have been detected or hypothesized in historical paintings where lead soaps were detected (statistic over about 150 paintings, as reported in 50 publications, cf. Table S1).

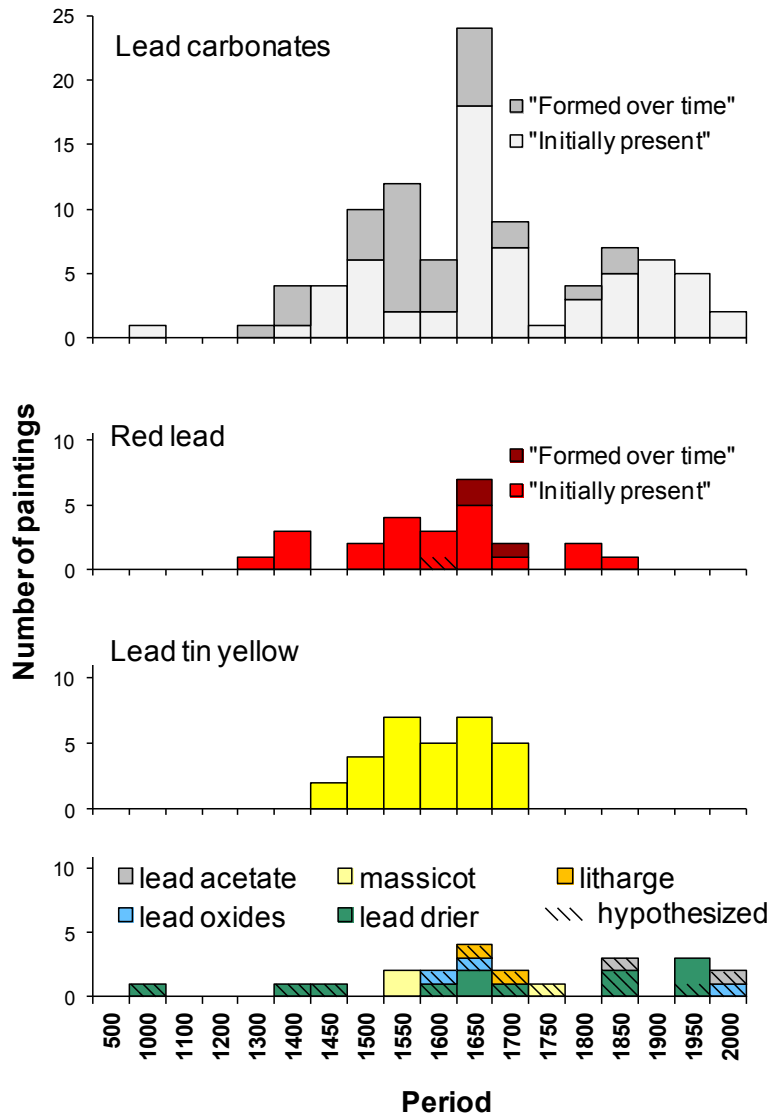


Figure 2: Temporal evolution of lead compounds detected or hypothesized in association with lead soaps, in historical paintings. Review over 150 paintings, from published studies, listed in Table S1

The most frequent lead compound in Fig. 2 is the family of lead carbonates. This refers to both the presence of “lead white” pigment and lead carbonates observed as remineralization products, in particular in protrusions. “Lead white”, also named “ceruse” has been synthesized since the Antiquity. The generic term “lead white” refers to different pigments with varying compositions and microstructures, including mainly hydrocerussite ( $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ ) and cerussite ( $\text{PbCO}_3$ ) in various

proportions (Gonzalez, *et al.*, 2016, Welcomme, *et al.*, 2007). Its continued presence over centuries reflects its continued use in paintings.

Minium ( $\text{Pb}_3\text{O}_4$ ), also named red lead in historical recipes, has been detected in association with lead soaps in many paintings, from ~1260-1280 in *The Westminster Retable*, English school, (Higgitt, *et al.*, 2003) to the 19<sup>th</sup> C. as in the portrait of João Luiz Lourenço, Ecomuseu Municipal do Seixal, Portugal (Devesa, 2012). In this case, and in others, it is not easy to determine precisely if minium was introduced as such in the painting and/or is a degradation product (see discussion below).

Lead tin yellow (LTY) was found in association with lead soaps in a more defined period, from early 15<sup>th</sup> C. in *"The Bad Chief"* by Master of Flémalle (Keune, 2005), till 1689 in *"The avenue of Middelharnis"*, by Meindert Hobbema (Higgitt, *et al.*, 2003). This corresponds well to the limited use of lead tin yellow in paintings throughout history.

Apart from these three pigments, few other lead-pigments were found associated with lead soaps, most recently in a late 19<sup>th</sup> C. historical chrome yellow oil paint tube (Monico, *et al.*, 2016).

In the bottom part of Fig. 2, five classes of lead compounds were merged: "litharge" ( $\text{PbO}$ , tetragonal form), "massicot" ( $\text{PbO}$ , orthorhombic form), a generic "lead oxides" class when the exact phase was not determined and lead acetate (another lead drier hypothesized only in a few 19<sup>th</sup> and 20<sup>th</sup> C, paintings). In 12 cases (over more than 170 paintings), a generic term "lead drier" has been hypothesized at the origin of the lead soaps. This figure also highlights the fact that while lead pigments (lead white, red lead or lead tin yellow) were undoubtedly identified in most cases, the detection and identification of lead driers is much more challenging, all the more so in the presence of another lead pigment (Noble, *et al.*, 2005, White & Kirby, 1994), and most of the time can only be hypothesized (dashed symbol). Globally, this figure shows a limited occurrence of lead driers as considered to be responsible for the formation of lead soaps in scientific publications.

A few other lead-compounds, e.g. lead potassium sulfates (palmierite,  $(\text{K},\text{Na})_2\text{Pb}(\text{SO}_4)_2$ ) (Boon, *et al.*, 2010, Cotte, *et al.*, 2008), pentalead tricarbonate dihydroxide oxide (plumbonacrite,  $\text{Pb}_5(\text{CO}_3)_3(\text{OH})_2\text{O}$ ) (Vanmeert, *et al.*, 2015), lead chloride (cotunnite,  $\text{PbCl}_2$ ) (Ordonez & Twilley, 1997), lead hydroxichloride (fiedlerite,  $\text{Pb}_3\text{Cl}_4(\text{OH})_2$ ) (Noble, *et al.*, 2000) were detected in a few cases and are not represented in Fig. 2. They are systematically identified as degradation products.

#### Are inorganic lead compounds initial ingredients and/or formed over time? [Subheading]

Fig. 2 also highlights many occurrences where lead compounds (in particular lead carbonates and minium) are thought to be degradation products, and not (necessarily) initial ingredients. This classification can be delicate and the same phase can be both an initial ingredient and the result of degradation, depending on the paint. When the first hypothetical schemes of formation of protrusions in paintings were proposed, a multi-stage process was envisaged where the reacting chemical would be lead white particles, which would dissolve, with formation of lead soaps aggregates and precipitation of minium (Boon, *et al.*, 2002). In the second stage, the aggregated masses would swell. Finally, mature protrusion with minium particles would remineralize, with the formation of new lead (hydroxy) carbonate.

Conversely, in other paintings, the presence of minium has been interpreted as intentionally introduced in the paintings (as a drier) and most probably as responsible for the formation of protrusions (Higgitt, *et al.*, 2003). Lead soaps inclusions were detected in 35 Northern European 13<sup>th</sup>-18<sup>th</sup> C. oil paintings containing red lead or LTY (type I). In 33 of them, lead carbonates (being as basic or neutral form) were found in the protrusions, but in only 5 of them lead white was present in the paint layers containing inclusions. Instead, red lead and LTY were present, alone or together, in 17

and 22 paintings, respectively. E.g. protrusions in the “Portrait of Charles I” by Daniel Mytens (Royale collection): *“Like the painting by van Bassen, the white translucent inclusions are embedded in a matrix of red earth pigment, but have unreacted red lead around them from which they originate”*. In the “Portrait of a young man” by Karel Dujardin: *“it is clear that here the lead soaps have formed from red lead both because of the location of the soap inclusions in the layer, and because in the same cross-section there is another layer (the upper part of the double ground) consisting of lead white and coarse black, but without red lead and without lead soap inclusions”* (Higgitt, et al., 2003). (Basic) lead carbonates found in the inclusions are supposed to come from the reaction of carbon dioxide (from the environment or formed by decarboxylation of fatty acid or soap) directly with red lead or LTY, or indirectly with lead soaps previously formed from reaction of oil with red lead or LTY (cf. (Higgitt, et al., 2003), in particular Table I and note 39)

A few years later, Boon et al. also analysed a LTY paint layer exhibiting protrusions. Fragments were sampled from the wings of the 15<sup>th</sup> C. Northern European *Sherborne Triptych* (Boon, et al., 2004). The particular distribution of tin and lead surrounding a metal soap aggregate appears as if *“lead stannate are pushed aside by the growing soap mass”*. Lead stannate grains seem intact and authors therefore reject the hypothesis that lead carboxylates would originate from the reaction of oil with lead stannate. Instead they say that: *“there is every reason to propose a second lead source that readily reacts with fatty acids. Possible candidates are lead oxide and minium (lead plumbate) [as residual compounds from the synthesis of LTY]. Lead white as an addition to the lead tin yellow paint is another possibility in view of the lead soap formation in a number of 17<sup>th</sup> century paintings, but lead white seems perfectly stable in the layer underneath the LTY”*.

These three cases further highlight the difficult distinction between pigments and driers, initial ingredients, introduced on purpose, or as impurities, and reaction products (usually qualified as degradation products when found in degraded area) and call for a careful study and reproduction of historical recipes.

## Recipes of lead-oil media, across History [Heading]

In parallel to the analysis of paint materials, the research of historical documentary sources is highly valuable and provides key information about the ingredients used, the quantities, the conditions of introduction (temperature, duration, exposure to sun light, etc) and the properties and use of the products. Recipes mixing oil and lead compounds can be found in various treatises, from the Middle Ages to 19<sup>th</sup> C. (Carlyle, 1999, Maroger, 1948, Mayerne, 1620-1646, Merrifield, 1999, Nadolny, 2008, Watin, 1773). 37 recipes are presented in supporting information (SI). Those provided by T. De Mayerne (Mayerne, 1620-1646) have been recently analyzed and presented in a synthetic way elsewhere (de Viguerie, et al., 2016). These recipes usually detail the pre-treatment of oil with lead compounds for different purposes, in particular for the preparation of ground, drying oils, gilding and painting on glass.

Written recipes are scarce until the 17<sup>th</sup> C. According to Sabin, the use of litharge and lead white as fat driers goes back to Antiquity, possibly the Egyptians. *“Galen, in the second century who speaks of the drying character of linseed and hempseed, also says that litharge and lead white are drying in their nature. Marcellus, in the fourth century, gives direction to put some oil in a new vessel and put it over a moderate fire; then add well ground litharge, sprinkling it little by little with the hand. Stir it constantly till the oil begins to thicken”* (Sabin, 1927).

The very first reports of recipes for oil paintings in Europe mention the use of lead driers (lead white), showing the fundamental role of lead driers for the early development of oil painting

technique (SI quot. 2 and 3) (Merrifield, 1999). The recipes differ by the choice of lead compound(s), additional ingredients (in particular water), the proportions, the duration, the temperature, but all fundamentally rely on the same principle: the reaction of lead compounds with oil. A kind of standard simple protocol appears which consists in mixing and heating litharge and oil to form “Fat oil” (“huile grasse”), according to P. Lebrun in 1635 (SI quot.15), “olio cotto”, according to Baldinucci or “olio coto” in Volpato Manuscript (SI quot.18 and 20), “boiled oil” in Paduan Manuscript, “fat Oyl” according to J. Smith in 1687 (SI quot.23). Interestingly, the names of these recipes insist on the presence of oil and the fact that it is heated but none mention the use of litharge. Only in (Mayerne, 1620-1646) a more explicit name “huile de litharge” is found (cf. Fig. 4). This recipe is also the basis of the formula proposed by Maroger as the first and the second lead media, attributed to Antonello da Messina and Leonardo da Vinci, respectively (quot.6 and 7, (Maroger, 1948)). Travelling across time and space, it is interesting to note that the use of litharge in paintings is also reported in Asian painting techniques, under the name “mitsuda-e”, based on the name « mitsudasou », which designates litharge (PbO) (SI quot.38). The technique consists in mixing vegetal oil and pigments with litharge. The recipe is assumed to originate from Persia, spread to China (known under the name “mituoseng”) in the 4<sup>th</sup> C. and then from China to Japan two or three centuries later (Uemura, *et al.*, 1954, Yoshida, 1941 ).

#### Lead-based ingredients [Subheading]

Fig. 3 shows the occurrence of the different lead compounds in the recipes given in SI, as well as published elsewhere (de Viguerie, *et al.*, 2016, Watin, 1773). The two peaks (1650 and 1800) are associated to the 29 recipes given by de Mayerne in 1620-1646 and 25 given by Watin in 1773 respectively.

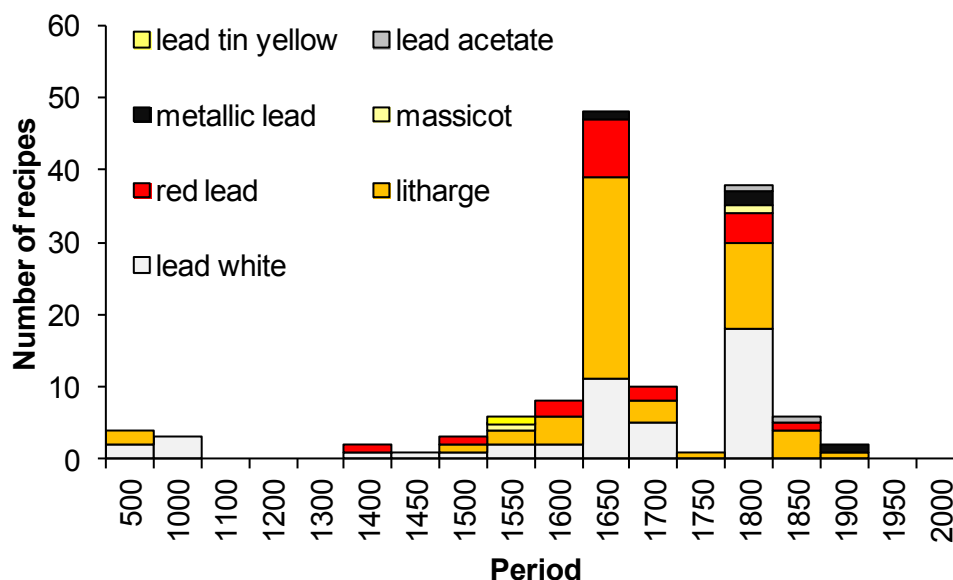


Figure 3: Temporal evolution of the number of recipes from paint treatises from Antiquity to 19<sup>th</sup> C., mentioning the use of various lead compounds. Statistic are based on texts given in SI as well as Watin 1773; de Viguerie, Payard *et al.* 2016.

Fig. 3 shows: i) the widespread use of lead driers across History, from Antiquity to modern times; ii) the predominance of litharge and lead white, followed by red lead, indistinctively of period; iii) in a

few recipes, the introduction of metallic lead (direct introduction or through the use of a lead container, e.g. SI quot. 37) and of LTY (SI quot.12). In agreement with Fig. 2, lead acetate appears only “recently”, at the 18<sup>th</sup> C. (quot. 30). Interestingly, *“the only lead compound, and indeed the only metallic drier, that was offered in 19th-century artists’ colormen’s catalogs as a separate product, until the last decades of the 19th century, was lead acetate. It was also the most frequently mentioned drier in the artists’ instruction books and handbooks. It is only through descriptions of the preparation of drying oils that we learn of the use of litharge, white lead, and red lead”* (Carlyle, 1999), again showing the poor visibility of lead driers, and litharge.

Lead driers have been intensively employed until the 20<sup>th</sup> C. where, considering their toxicity, they were progressively excluded from paint and plastic industries (Skalský, 1976). In the U.K. they were completely eliminated by July 1987 (Tumosa & Mecklenburg, 2005). Interestingly, in 1850 Michel-Eugène Chevreul -who was the first to explain the reaction of saponification in 1823- is asked by the French Academy of Science to determine if lead white could be efficiently substituted by zinc oxide, a less toxic drier. He reports detailed studies of experimental follow-up of drying (Chevreul notes that this is not, from a chemical point of view a “drying”, which would mean removal of humidity, but more an oxidation, since oxygen is consumed during the full process) of linseed oil, with different metal-based compounds (mainly litharge, manganese peroxide, antimony oxide, lead white and zinc white). As an example, he observes that a layer of linseed oil will dry: in 99 days without treatment, in 41 days if it has been “boiled” (here again, Chevreul underlines that this term is inappropriate from a chemical point of view) and in only 2 days if oil has been primarily “boiled” with 1/10 (mass) of litharge (Chevreul & France, 1850).

Not shown in Fig. 3 but shown in SI, a single recipe could involve the introduction of many different lead compounds (e.g. SI quot.13 and 19). Studying the archives of Winsor & Newton, Carlyle et al. show that up to four different sources of lead (litharge, red lead, lead white and “sugar of lead” = lead acetate trihydrate) can enter into the composition of a commercial ground preparation, dated from 1871 (Carlyle, *et al.*, 2008).

It has to be underlined that all the recipes refer as oil pre-treatment. The lead drier is introduced and reacts with the oil to form lead soaps; if the kinetics is slow, e.g. at ambient temperature, the mixture is then settled down and the solid part removed. On the contrary, if the mixture is submitted to heating step, then the kinetics is faster and the lead compound is usually not present any more at the end of the process. Indeed one can easily understand the advantage of introducing soluble lead soaps, vs. insoluble yellow litharge or lead white.

#### Introduction of water [Subheading]

Some recipes mention the addition of water in the lead-oil mixture during heating (e.g. SI quot.29 or the recipe by de Mayerne shown in Fig. 4A). According to Maroger this would have been proposed by Leonardo da Vinci (SI quot.8). Water allows a control of the temperature and avoids burning oil. The resulted medium is white (cf. Fig. 4B) while “boiled oils” prepared without control of temperature are usually brown, as shown in our reconstructions (de Viguierie, *et al.*, 2008). The color of the drying oils has indeed an impact on the use which can be made of it, darker ones being limited to shades and backgrounds (Carlyle, 1999). Interestingly, the study of equivalent lead plaster recipes in more than 40 pharmaceutical treatises shows a similar evolution, from dry processes in Antiquity and Middle Ages (ending into black plasters) to wet processes (ending into white plasters), during the 18<sup>th</sup> and 19<sup>th</sup> C. (Cotte, 2004). The transition from dry to wet processes probably occurred during the 17<sup>th</sup> C. In Lemery’s pharmacopeia, the majority of recipes includes an aqueous ingredient

(Lemery, 1764). Diderot gives a very detailed explanation of the advantage of adding water in the preparation of “lead plaster” (SI quot.39).

#### Duration of the different steps [Subheading]

Durations of the protocols are extremely variable. For short steps the time is scarcely defined (few exceptions: “while you can say three paternosters”, SI quot.4), but typical recipes such as “fat oil” can be reproduced within 1 hour under heating (Cotte, *et al.*, 2006). The duration of longer processes are indicated more often (weeks, months, e.g. quot.21; one Summer (Watin, 1773)). In the description of ground preparation from Winsor & Newton mentioned above, the “1<sup>st</sup> Colour oil” is recommended to be prepared and aged 6-12 months prior to use since, “*by being kept it acquires a glutinous quality, necessary to prevent oil of the 1<sup>st</sup> Colour from running through the back of the canvas and causing it to have a stained appearance*” (Carlyle, *et al.*, 2008). These different examples show the very large range of kinetics, in the preparation of lead media.

Oil processing (e.g. the introduction of lead driers, the temperature, and the addition of water) completely modifies the chemical and physical properties of oil and of its following mixture with pigments. This complex processing underlines the importance to reproduce such complex compositions and to take into account the different ways lead compounds could enter into the paint composition. Carlyle conducted a huge study trying to reproduce as accurately as possible historical oil painting materials (Carlyle, 2006, Carlyle, *et al.*, 2008). She notes: “*Clear differences in the handling properties of lead white paint could be distinguished according to the lead compound used to treat the oil prior to use (e.g. litharge (lead (II) oxide), lead acetate and lead subacetate), and the degree of heat applied to the oil*” (Carlyle, 2006). Unfortunately, establishing the pretreatments undergone by the oil in historical paintings thanks to multi-analytical chemical approaches turns out to be extremely challenging (Bonaduce, *et al.*, 2012, Bonaduce, *et al.*, 2012).

#### Confrontation of historical texts with experimental observations [Heading]

A good way to get clues about painters’ gestures, in addition to the study of their artworks is the reproduction of painting materials by following historical recipes. This gives fundamental ways to follow short-term, but also mid-term and even long-term evolutions of painting materials, and in particular to monitor reactions between ingredients, during paint preparation as well as during natural and artificial ageing. These experimental reproductions can be used to see at which speed (from minutes to years) metal soaps can form and which factors (ingredients, type of pigmentation, mixtures or pure pigmentation, ratio pigment/oil, environmental conditions in particular presence of water, temperature, etc) influence the saponification kinetics. The study and reproduction of historical recipes is fundamental to assess these different aspects, and determine if the painter prepared the soaps him/herself on purpose or if they appeared naturally. Different works report the study of reactions of lead compounds with organic binders (usually oil, sometimes egg yolk, beeswax or resin), ranging from the preparation of simple binary mixtures, up to the accurate reproduction of historical recipes (Bonaduce, *et al.*, 2012, Bonaduce, *et al.*, 2012, Boon, *et al.*, 2006, Carlyle, 2006, Carlyle, *et al.*, 2008, Catalano, *et al.*, 2014, Cotte, *et al.*, 2006, Cotte, *et al.*, 2007, de Viguierie, *et al.*, 2016, Duce, *et al.*, 2013, Erhardt, *et al.*, 2005, Mazzeo, *et al.*, 2008, Mecklenburg & S., 2001, Meilunas, *et al.*, 1990, Osmond, 2014, Pallipurath, *et al.*, 2015, Pratali, 2013, Salvadó, *et al.*, 2009). An interesting observation is given by Mazzeo *et al.* who reported the FTIR analysis of model paintings prepared by mixing oil and egg yolk with 42 different pigments, among which eight lead-based compounds after 10 years of natural aging (Mazzeo, *et al.*, 2008). The study revealed the



presence of lead carboxylates for all the mixtures with lead-based compounds, in particular those with litharge and minium. It was additionally observed that lead carbonates form when these two particular compounds are used, both with oil and with egg yolk. This result is extremely important since it highlights the fact that the ingredients presently detected in paintings were not necessarily introduced into the painting at its creation. Lead carbonates are extensively detected in paintings; it is important to keep in mind that they can be the product of the evolution of another lead based ingredient (e.g. lead oxides). It could be related to the many historical paintings where lead carbonates are thought to be remineralization products, in particular in lead soaps protrusions (Fig. 2).

Reproduction of “Olio cotto” recipes [Subheading]

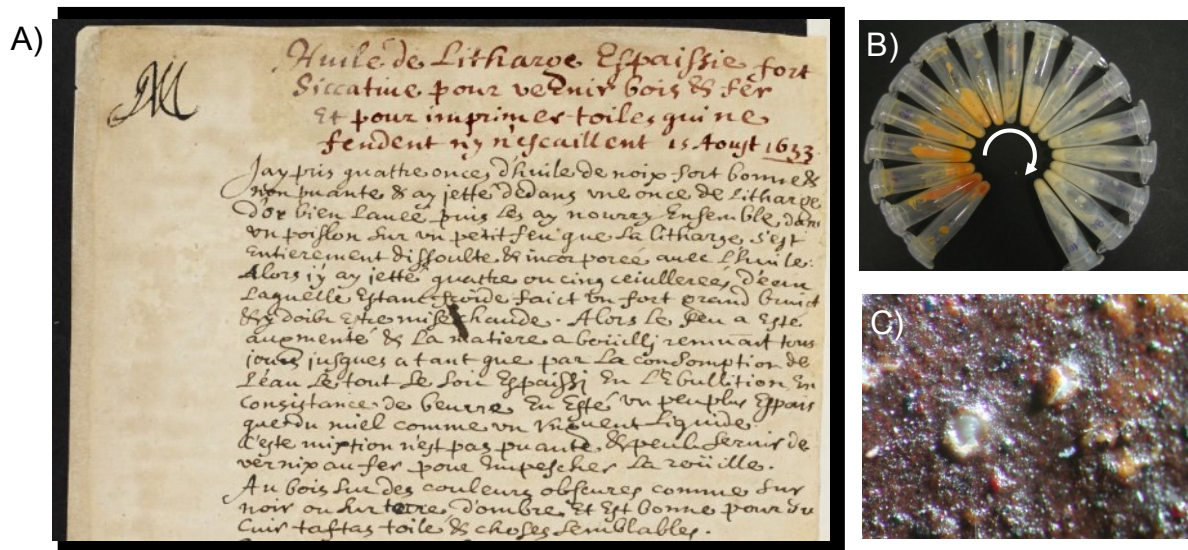


Figure 4: A) Folio 28v, from De Mayerne (© The British Library Board, Sloane 2052 fol.28v.) « Huile de litharge epaissie fort siccativ pour vernir bois et fer et pour imprimer toiles, qui ne fendent ni ne s'écaillent, 15 aout 1633. J'ay pris quatre onces d'huile de noix fort bonnes non puantes et ay jetté dedans une once de Litharge d'or bien lavée, puis les ay nourries ensemble dans un poeslon sur un petit feu que la litharge s'est entièrement dissoute et incorporée avec l'huile. Alors j'y ai jetté quatre ou cinq cuillerées d'eau laquelle estant froide fait un fort grand bruit et y doit estre mise chaude. Alors le feu a été augmenté et la matière a bouilli remuant tousjours jusques à tant que par la consommation de l'eau le tout se soit epaissi en Ebullition en consistance de beurre en Esté, un peu plus espais que du miel, comme un unguent liquide. Ceste mixtion n'est pas puante. Et peult servir de vernix au fer pour empescher la rouille. Au bois sur des couleurs obscures comme sur noir ou terre d'ombre et est bonne pour du cuir, taftas, toile, et choses semblables. » “Thickened, rapidly drying, litharge oil to varnish wood and iron and to prime canvas, which do not split or crack, 15<sup>th</sup> August 1633. I took four ounces of good quality not smelly walnut oil and threw in one ounce of well washed gold litharge, then I stirred them together in a pan on a low heat so that the litharge is completely dissolved and mixed with the oil. Then I added four or five spoonfuls of water, which if cold would spatter widely, and so must be added warm. Then the heat was increased to bring the mixture to boiling point, while stirring, until the water has been consumed. The mixture will thicken when boiled to have a consistence of soft butter, a little thicker than honey, like a liquid unguent. This mixture does not smell bad. It can be used as a varnish on iron to prevent rust, on wood on dark colours such as black or umber and is good for leather, taffetas, canvas, and similar materials.” B) Evolution of color during the reaction of litharge with walnut oil and water, at 100°C. C) Observation of white protrusions of a model paint prepared with “huile de litharge” following folio28v recipe (from (Cotte, et al., 2007)).

In order to mimic more accurately historic recipes, we reproduced a lead-based medium adapted from the Formula for the second lead medium, (SI quot.7) and the Folio 28v of T. Turquet de Mayerne’s treatise (Mayerne, 1620-1646) (Fig. 4A). The details can be found elsewhere (Cotte, et al.,

2006). The visible observation of the mixture shows the progressive disappearance of the litharge orange color (Fig. 4B); FTIR spectra of pure walnut oil and of the medium at the end of the preparation are shown in Fig. 5a and 5b respectively. These two spectra were acquired with different instruments (Cf. supplementary information). For readability, the Y scale for spectrum 5b was multiplied by five, in order to reach equivalent intensity on the  $\nu(\text{CH})$  signal at  $\sim 2900\text{cm}^{-1}$ . A detailed description of the main FTIR peaks of such partially saponified oil can be found in (de Viguerie, *et al.*, 2016). The grey Regions Of Interest (ROIs) highlight the main variations. Various C=O species such as esters, acids, ketones, anhydrides, aldehydes absorb in the ROI1 region. Here the decrease of the intensity in this region is mainly due to the consumption of esters. The carboxylate asymmetric C=O stretching signal appears in ROI2 (peaked at  $1522\text{cm}^{-1}$ ) while the symmetric stretching appears in ROI3 (peaked at  $1401\text{cm}^{-1}$ ). As previously reported, FTIR can be used to quantitatively monitor the saponification rate (Cotte, *et al.*, 2006). We showed in particular that the use of water and of heat ( $100^\circ\text{C}$ ) dramatically increases the speed of oil saponification.

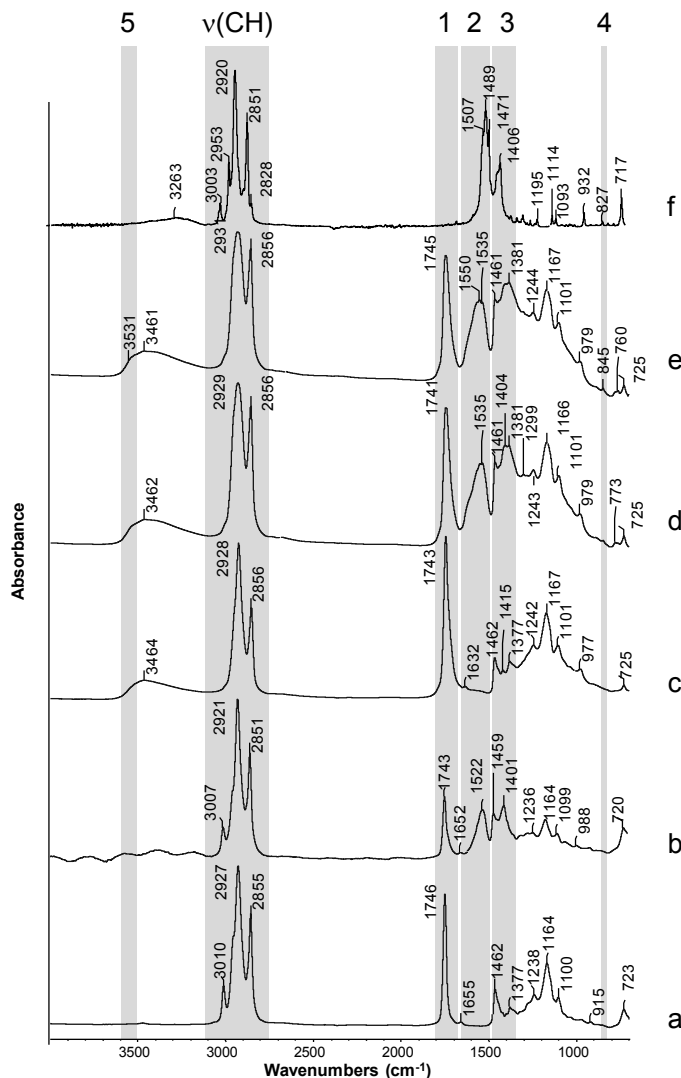


Figure 5: FTIR spectra: a) pure walnut oil; b) final product of the preparation of “huile de litharge”, following De Mayerne f28v recipe; c) – e) “Walnut oil – litharge” system let one month a room condition. Three average spectra were calculated, based on ROI intensity maps displayed in Fig.6: c) average “oil-ROI3” (over 928 pixels), d) average “particles-ROI3” (over 155 pixels) and e) average “particles-ROI4” (over 21 pixels). Spectra are baseline corrected, plotted with common scale (with an offset) except for spectrum b) which Y scale has been multiplied by 5 for readability (to reach

equivalent intensity on the  $\nu(\text{CH})$  signal). Grey rectangles represent region of interest (ROIs) selected to map some specific bands: 1: 1785-1692, 2: 1600-1483, 3: 1432-1339, 4: 855-834, 5: 3582-3516 and  $\nu(\text{CH})$  3041-2780 $\text{cm}^{-1}$ . f: reference spectrum of lead oleate, from (Robinet & Corbeil-a2, 2003), kindly provided by L. Robinet.

The reconstruction of a similar “leaded oil” (linseed oil boiled for 2 hours in the presence of litharge) by Brinkman allowed proposing that Van Eyck used such a lead treated oil for his isolation layers in the “*Het Lam Gods*” retable and that van der Weyden employed a similar lead treated oil based medium in an isolation layer above his under drawing in “*The Descent from the Cross*” (Ferreira, et al., 2006). The same reconstructions were reanalyzed with FTIR by Ferreira et al. after 25 years of natural ageing and demonstrated the presence of lead carboxylates. They are said to “*result from the reaction of the oil and the lead oxide during the last 25 years*” (Ferreira, et al., 2006). Considering the way leaded oil was prepared however, there is a high probability that most of these soaps were already present at the time of the preparation of the reconstruction. Interestingly, the authors also note that “*When the leaded oil is mixed with glue the concentration of lead carboxylates is lower and its detection by FTIR proves difficult. The relative concentration of lead in the emulsion is also very low in the SEM-EDX mapping data. This is a particularly important finding because it means that leaded oil addition by painters may be obscured or an absence of lead in an isolation layer can be misinterpreted*”.

Meilunas in his pioneer FTIR analysis of aged paint binders, reports FTIR spectra acquired on model paint samples (the Fogg test plates, prepared by R. J. Gettens, between 1929 and 1933), as well as on fragments from two Italian renaissance paintings of historic interest (Meilunas, et al., 1990). One of them is a wood panel, probably painted between ~1480 and 1497 by Antonio da Saliba, nephew of Antonello da Messina and depicting the “*Enthroned Madonna*”. The white sample from the base of the Madonna’s throne presents characteristic spectral signatures of lead white and of an oil-based medium, which was an important discovery since “*it was one of the first analyses of media from a painter so close to the origins of [oil painting] in Italy*”. But, even more interestingly, spectra also exhibit peaks characteristic of lead carboxylates, very similar to those observed on the Fogg reference mixture of linseed oil with lead white (1:1), artificially aged at 120°C for one day and in agreement with historical recipes (cf. quot.7, *The formula for the first lead medium*, attributed to Antonello da Messina, as proposed by Maroger).

Similarly, the “mitsuda-e” recipe (quot.38) could explain the presence of lead carboxylates found in 2008 in the famous Bamyian wall paintings dating from the 7<sup>th</sup> to 9<sup>th</sup> C., and being one of the earliest known uses of oil painting (Cotte, et al., 2008, Taniguchi, et al., 2008).

#### Heat vs. time [Subheading]

Since “boiled oil” (“*olio cotto*”) seems to have been a standard recipe, it was also interesting to follow the reaction of oil with litharge in softer conditions (room temperature, without water; similar to quot.21). For this purpose, particles of litharge were deposited on a droplet of walnut oil, and let in room conditions (cf. the description of “*Walnut oil – litharge*” system in Supplementary information). FTIR maps were acquired at  $t=0$  and after one month. Average FTIR spectra are shown in Fig. 5a (oil at  $t=0$ ) and Fig. 5c-e (average over different parts of the system, after one month) and FTIR ROI maps of the one-month system are plotted in Fig. 6. The map of  $\nu(\text{CH})$  stretching bands shows a higher intensity in the particles region. This may be interpreted as a higher density of fatty chains in this region. Similarly, the ROI1 map (mainly C=O ester) shows higher intensities in this region; however, the calculation of the ratio map ROI1/ $\nu(\text{CH})$  shows that the relative amount of

esters clearly decreases in the vicinity of particles. Concomitantly, ROI2 map (here shown after normalization by  $\nu(\text{CH})$  ROI intensity) and ROI3 map show an increase of carboxylate signals in this region. From ROI3 map, two averaged spectra were calculated: average “oil-ROI3” (over 928 pixels, out of the particles, Fig. 5c) and average “particles-ROI3” (over 155 pixels, on the particles, Fig. 5d) (cf. Fig. 6 for explanations about their calculation). The comparison of these two spectra supports the results from the observation of the maps: less esters and more carboxylates close to the particles. Comparing these spectra with the spectrum of fresh oil (Fig. 5a) reveals additional features, characteristic of drying reactions, which can be observed everywhere (close or far from the particles): increase of hydroperoxides, alcohols and acids  $\nu(\text{OH})$  at  $\sim 3400\text{cm}^{-1}$  and disappearance of  $\nu(\text{CH})$  of unconjugated cis double bonds at  $\sim 3010\text{cm}^{-1}$ . Comparing spectrum 5d (average “particles-ROI3”) with spectrum 5b (spectrum at the end of the preparation of de Mayerne’s “huile de litharge”) shows a higher intensity of the peak in ROI3. It can be interpreted as the additional presence of lead carbonate, contributing through an intense  $\nu_3$  mode at  $\sim 1400\text{cm}^{-1}$  (Brooker, *et al.*, 1983). For comparison, a reference of pure lead oleate is shown in Fig. 5f. This interpretation is supported by the presence of a small peak at  $845\text{cm}^{-1}$  which can be attributed to  $\nu_2$  mode lead carbonate (intensity mapped in Fig. 6-ROI4). The average spectrum over few pixels with high ROI4 intensity (“particles-ROI4”, Fig. 5e) further confirms this result. A very weak shoulder can be seen at  $3531\text{cm}^{-1}$ , in particular when superimposing spectrum 5c with 5d and 5e. It can be assigned to a  $\nu(\text{OH})$  mode, in a lead hydroxide group, as seen in the spectrum reference hydrocerussite (Brooker, *et al.*, 1983) (intensity mapped in Fig. 6-ROI5). However, this signal is very weak, and would require to be further confirmed by  $\mu\text{XRD}$ . In conclusion, in agreement with what was observed by Mazzeo *et al.* (Mazzeo, *et al.*, 2008), the reaction of litharge with oil at room temperature leads to the formation of lead carboxylates and lead carbonates, but we prove here that this occurs in very short time (already in one month), similar to recipe quot.21.

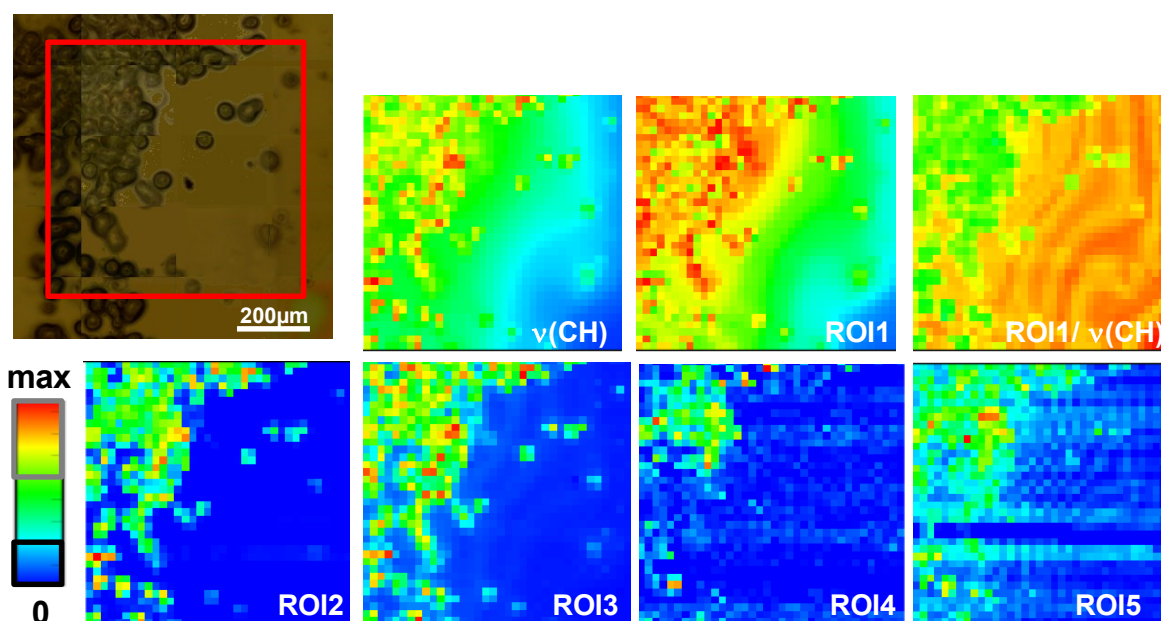


Figure 6: visible light picture and  $\mu\text{FTIR}$  maps of the “Walnut oil – litharge” system after one month at room conditions. Integrated signal over the ROI shown in Fig. 5, in colour scale. For each map, the red colour corresponds to the highest ROI intensity, and the blue (minimum) is fixed to 0. Map conditions: spectra are averaged of 64 scans, spectral resolution:  $8\text{ cm}^{-1}$ , beam size and pixel size:  $20\times 20\mu\text{m}^2$ . The black rectangle displayed on the colour scale represents the

colour of pixels selected to calculate the spectrum “oil-ROI3” (Fig. 5c) (automatic selection of pixels with intensity lower than 2.4% of maximum intensity, in ROI3). The grey rectangle displayed on the colour scale represents the colour of pixels selected to calculate spectra “particles-ROI3” (Fig. 5d) and “particles-ROI4” (Fig. 5e) (automatic selection of pixels with intensity higher than 60% of maximum intensity, in ROI3 and ROI4 respectively).

## When a friend becomes a foe: possible risks associated with lead driers

### [Heading]

#### Historical warnings with respect to the use of lead driers in paintings [Subheading]

The risks associated with the use of lead driers have long been recorded (Carlyle, 1999). In French, the protrusion phenomenon has been described since more than 50 years, as “lithargeage” but this word does not seem to be used in English (with only few exceptions (Glanville, 1995, Noble, *et al.*, 2000)). According to Bergeon and Faillant-Dumas, “lithargeage”, which gives the paint surface a granular aspect, is associated to insufficient grinding of the ceruse used in the ground layer or the litharge used to make oil more siccative (Bergeon & Faillant-Dumas, 1980). Earlier, in 1830, Mérimée indicates about the preparation of ground layers: *“Formerly, the first priming was made with dark red, mixed with umber, or with pure umber; and some sixty years since, it was supposed that the drying of this colour would be quickened by mixing it with litharge; but it has been discovered that pictures painted on these sorts of preparations, in a few years have their surfaces covered with a multitude of little grains like sand; and thus proving that the litharge was badly prepared.”*<sup>1</sup> [1: had the litharge been very finely ground, that evil effect could not have occurred]. *At the present days, the artists are more careful in such essential matters; and the colourmen, for their own sakes, are excited to prepare their canvasses with more attention, for any negligence in this essential matters would ruin their trade”* (Mérimée, 1981). A too coarse grinding of litharge seems to be responsible for the granular aspect of the paint surface. Many recipes insist on the importance to grind driers well (e.g. *“litharge or glass, finely ground with water”*, SI quot. 18), to mix them well with oil, to avoid aggregation and excessive heating. They advise to avoid having residual litharge in the mass after preparation (SI quot.7). A good way to avoid such residual presence of un-reacted driers is to place lead compounds in a rag during cooking (SI quot. 14, 15, 20). Field recommends to dissolve lead acetate prior to its use (Carlyle, 1999). As detailed in (Carlyle, 1999, Tumosa & Mecklenburg, 2005), many historical texts also underline the risks associated with the excessive use of driers. The misuse of driers is particularly visible on 19 and 20<sup>th</sup> C. works of art showing dramatic defects, sometimes appearing a few years after their creation; painters started to use industrial formulation and were less cautious and less educated on the paint properties.

#### Experimental observation of formation of protrusions [Subheading]

Eleven years ago, we reproduced the recipe folio28v from De Mayerne to paint a model portrait, mimicking a 17<sup>th</sup> C. anonymous portrait, under restoration at the French “Institut National du Patrimoine”. The original painting was suffering from massive presence of protrusions, and reproducing the painting was a way to follow in real time the possible formation of protrusions. “Huile de litharge” was prepared following Folio28v recipe (see above), but using a coarsely grind litharge. It was then mixed with ochre and applied on different substrates. Some part of the ochre-medium was applied on a canvas, another part was applied on a Melinex polymer foil (see sample description in Supplementary Information). Very surprisingly, while protrusion formation is sometimes said to be a very slow process (Higgitt, *et al.*, 2003), protrusions were observed on the model paintings, deposited on both canvas and polymer substrates, after only one month (Fig. 4C).

The protrusions from canvas model painting were sampled and analyzed by synchrotron based  $\mu$ XRF and  $\mu$ FTIR after 3 months (Cotte, *et al.*, 2009) and after one year (Cotte, *et al.*, 2007), and revealed an incredible similarity in terms of elemental and chemical composition with respect to protrusions sampled from the historical portrait. The principal dissimilarity was the color: the protrusions from the original painting were orange (suggesting the presence of minium) while the ones from the model painting were white. It was decided to re-analyze the protrusions from the model painting after 9 years of natural ageing using SR  $\mu$ FTIR and  $\mu$ XRD. SR  $\mu$ XRD is extensively used (in 2D or 3D) to get access to the phase micro-compositions of painting fragments and artistic material in general. It offers a step further along the path leading to the identification of artistic ingredients and degradation products. In particular, we were interested in determining the possible presence of residual litharge or other lead phases. A new fragment containing a protrusion was taken from the Melinex model painting. A 4 $\mu$ m thin section was prepared from the non-embedded fragment, following a procedure recently developed (Pouyet, *et al.*, 2014), and analyzed with  $\mu$ FTIR and  $\mu$ XRD at beamlines ID21 and ID13 of the ESRF (see sample description in Supplementary Information).

$\mu$ FTIR chemical maps (Fig. 7) highlight specific areas over which averaged FTIR spectra were calculated (Fig. 8). As observed previously, the protrusion presents features typical for a partially saponified oil and shows a high concentration of carboxylates (Fig. 7-ROI2). This map was used to define a set of pixels over the inclusion, from which the average FTIR spectrum was calculated (Fig. 8c). The signal from kaolinite is completely absent in this area, confirming that the protrusion grew pushing the surrounding medium (Fig. 7-kaolinite). FTIR spectrum in Fig. 8d is the average of pixels automatically selected on kaolinite hot spots, with intensity higher than 60% of maximum intensity. Carboxylates are also present in the surrounding matrix (Fig. 7-ROI2). Five areas were selected on this map to calculate the average FTIR spectrum in carboxylate-rich surrounding matrix (Fig. 8b). As observed above with the PbO particles on an oil droplet, the comparisons ROI2 vs. ROI3 maps and spectrum 8b vs. 8c demonstrate the additional presence of lead carbonates in the protrusions.

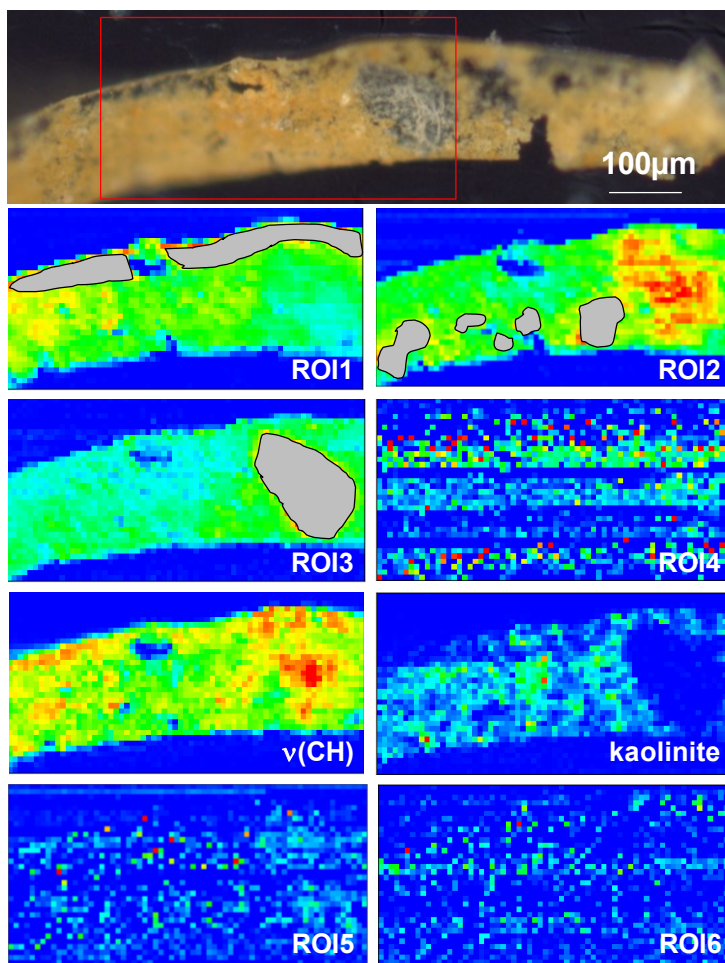


Figure 7: visible light picture (top) and  $\mu$ FTIR 2D maps of a thin section from a model paint prepared following de Mayerne recipe folio28v and exhibiting a white, transparent protrusion in a yellow medium. Map size:  $462 \times 231 \mu\text{m}^2$ , beam and pixel size:  $7 \times 7 \mu\text{m}^2$ , average of 60 scans, spectral resolution  $8 \text{cm}^{-1}$ . The areas surrounded by black lines represent the different set of pixels selected to calculate average spectra (cf. Fig. 8). ROI1 to ROI5 and v(CH) as in Fig. 5; ROI kaolinite:  $3724\text{--}3584$  and ROI6:  $1052\text{--}1039 \text{cm}^{-1}$ . Colour scale as in Fig. 6.

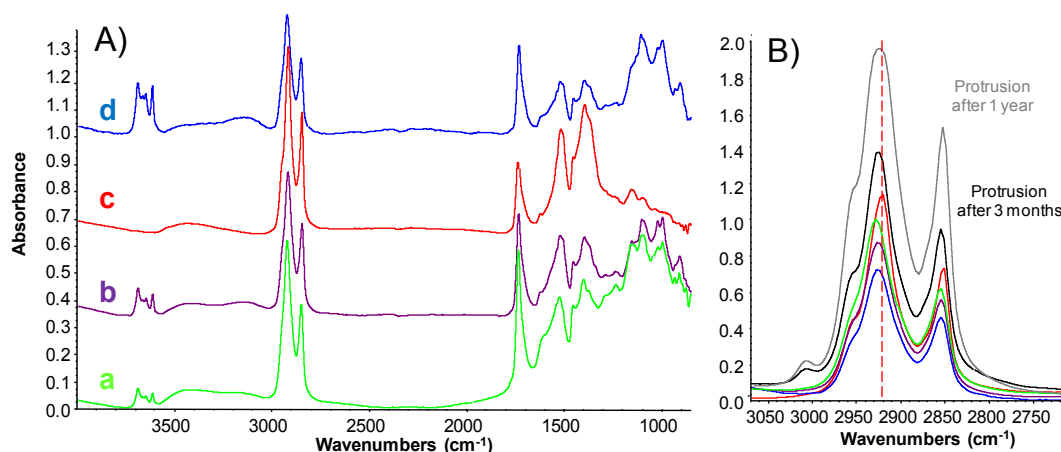


Figure 8: A) baseline corrected FTIR spectra averaged over areas shown in Fig. 7: a) ROI1 map: superficial layer with high ester intensity, b) ROI2 map: high carboxylate intensity, excluding the protrusion region, c) ROI 3 map: high carbonate intensity, corresponding to the protrusion region. For these three maps, areas were selected with the brush tool using PyMca ROIImaging software over regions of interest, and not specifically based on signal intensity. d) ROI kaolinite map (average over the pixels automatically selected with intensity higher than 60% of maximum intensity). B) Zoom on v(CH) signal and comparison with the average spectra acquired on protrusions after 3 months and 1 year.

The FTIR map of ROI1 (esters and acids mainly) shows a higher intensity on the surface of the painting (Fig. 7 ROI1). The area shown on this map was used to calculate the average spectrum shown in Fig. 8a. Both maps and spectra show that inorganic components (in particular kaolinite) are less present in this region. This could be explained by some decanting effects and/or migration of some oil components to the surface. Such “oil separation” effects were also noted by Carlyle et al. in one of their reconstructions of Winsor and Newton ground preparation, giving the false impression of a deliberately applied intermediate layer while the studied reproduction was made of a unique ground layer (Carlyle, *et al.*, 2008).

A detailed study of the  $\nu(\text{CH})$  signal (Fig. 8B) reveals in the protrusion a red shift of the asymmetric and symmetric stretching peaks, which are also sharper than in the surrounding matrix. Such intense and sharp peaks have already been observed on protrusions from historical paintings (Higgitt, *et al.*, 2003) and can be related to the concentration of saturated fatty soaps (possibly palmitic and stearic acids) in protrusions. For comparison, averaged spectra over protrusions and in the surrounding matrix for the maps acquired after three months and one year are also plotted (Fig. 8B and Fig. 9). The global observations after three months, one year, and nine years are basically the same: higher carboxylate vs. ester ratio in the protrusions and concentration of lead carbonate in the protrusions. Besides, after nine years, additional changes such as drying reaction features (monitored through the decrease of  $\nu(\text{CH})$  of unconjugated cis double bonds at  $3006\text{cm}^{-1}$ ) and fatty chain organization (red shift at  $2921\text{cm}^{-1}$ ) can be noticed. These phenomena seem to be a slow process, compared to the “fast” formation of protrusions.

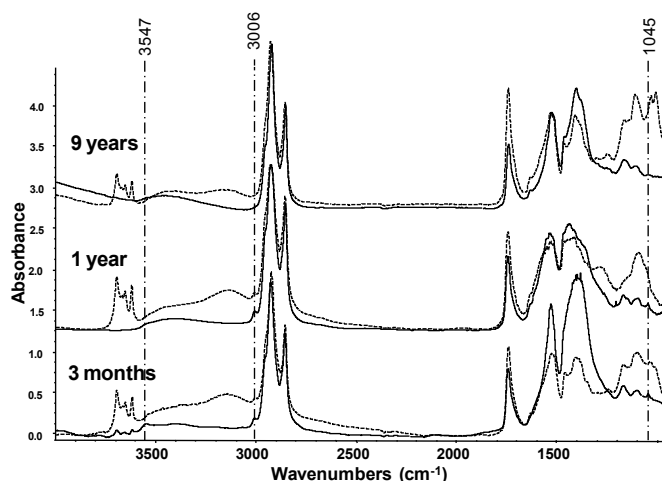
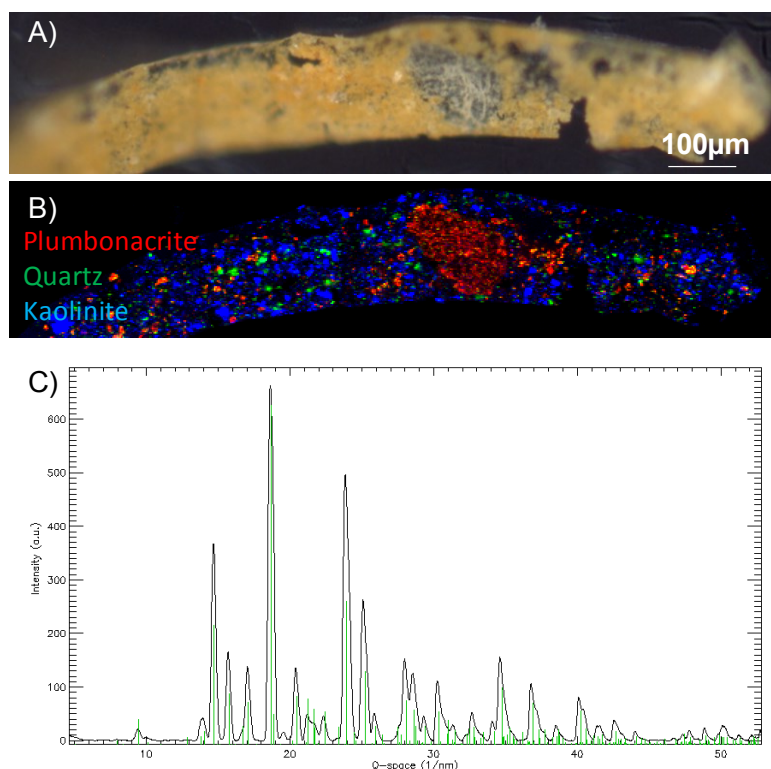


Figure 9: Averaged FTIR spectra from 2D maps acquired on thin sections of model painting prepared following De Mayerne recipe folio28v. Averages were calculated over protrusions (continuous line) and in the yellow surrounding matrix (dotted line), on 3-months, 1-year and 9-years old model painting.

The same thin section of 9-years old model painting was mapped using  $\mu\text{XRD}$  (Fig. 10). Kaolinite and quartz were easily identified and are present in the yellow medium. The only lead phase identified was pentalead tricarbonate dihydroxide oxide ( $\text{Pb}_5(\text{CO}_3)_3(\text{OH})_2\text{O}$ , PDF 19-0680), controversially named “synthetic plumbonacrite” (Corbeil & Sirois, 2007). This phase is rarely found in paintings. It was identified in commercial grounds from Lefebvre-Foinet (Paris), used in several paintings by the Canadian artist Jean-Paul Riopelle (1923-2002). It enters into the composition of a type of lead white (“modern lead white”) developed in the first half of the 20<sup>th</sup> C (Corbeil & Sirois, 2007). It was



detected in model paints made by mixing oil and egg yolk with lead white, naturally aged for at least 8-10 years (Salvadó, *et al.*, 2009). It also has been recently identified and mapped by 3D SR- $\mu$ XRD as an intermediate phase involved in the degradation of red lead in protrusions sampled from “*Weat stack under a cloudy sky*”, by Van Gogh (Vanmeert, *et al.*, 2015). The core of this latter protrusion is orange and contains minium. Two main hypotheses are proposed: plumbonacrite could derive from minium, or from PbO. PbO was not detected in Van Gogh’s painting. Alternatively, it is proposed to result from the photoreduction of minium. In the present model painting, the explanation of the formation of plumbonacrite can be directly ascribed to the carbonation of PbO, since no minium was introduced in our case.



**Figure 10:** A) visible light picture and B)  $\mu$ XRD maps of the 9-year old protrusion, showing the distribution of plumbonacrite, quartz and kaolinite. Map size:  $600 \times 150$  steps of  $2\mu\text{m}$ . The crystalline phase distribution maps are the result of diffraction pattern fitting. The structural parameters of Plumbonacrite (doi:10.1180/002646100549887), quartz (doi:10.1107/S002188989901643X) and kaolinite (doi:10.1346/CCMN.1993.0410613) were fixed during fitting while peak shape parameters were constraint. The scaling factor of each phase was the fit parameter taken for the distribution maps. C) Diffraction pattern obtained as the "maximum intensity" (superimposed) pattern of all pixels from the plumbonacrite map with intensity higher than 50% (1143 pixels). Green lines are from plumbonacrite (<https://dx.doi.org/10.1180/002646100549887>).

XRD is more specific than FTIR to identify plumbonacrite. This phase can also be distinguished from cerussite and hydrocerussite using FTIR (Brooker, *et al.*, 1983). Basically, a peak at  $\sim 3530\text{cm}^{-1}$  is characteristic of a lead hydroxide. Cerussite is characterized by the absence of this peak but shows very intense peaks at  $1052$  and  $838\text{cm}^{-1}$ . The peak at  $\sim 840\text{cm}^{-1}$  is very weak for hydrocerussite and plumbonacrite. The spectrum of hydrocerussite exhibits a medium peak at  $1045\text{cm}^{-1}$ , which is very weak for plumbonacrite. In summary, if the different lead (hydroxyl) carbonates are present alone, they can be identified. If they are present together, their accurate identification is challenging. In particular, the identification of plumbonacrite is less straightforward since it relies on the absence of two peaks and not on the presence of a specific peak. In the FTIR spectrum averaged over the 9-year

protrusion (Fig. 9), a very weak shoulder can be seen at  $\sim 3536\text{ cm}^{-1}$ , and the absence of peaks (at  $1045\text{ cm}^{-1}$  and  $840\text{ cm}^{-1}$ ) is in agreement with the presence of plumbonacrite. The maps of these three peaks (Fig. 7 ROI5, ROI6 and ROI4 respectively) support this conclusion. Without the information provided by XRD however, the identification of plumbonacrite would have been very difficult due to the very low signal-to-noise ratio. As a comparison, in Fig. 9, the average spectra over the 3-month and 1-year protrusion show a strong peak at  $3548\text{ cm}^{-1}$  and a weak peak at  $\sim 3538\text{ cm}^{-1}$  respectively, attributable to lead hydroxide, and a medium peak at  $1045\text{ cm}^{-1}$ . No peak is observed at  $\sim 840\text{ cm}^{-1}$ , however the FTIR signal is very noisy in this region. In conclusion, we can hypothesize that in younger protrusions, hydrocerussite was present, but we cannot exclude that plumbonacrite was present as well. These two phases are known to be products from the reaction of carbon dioxide on litharge in the presence of water (Martinetto, *et al.*, 2003). This example shows that FTIR can provide a preliminary screening of the presence and location of these lead oxy/hydroxy/carbonates, but XRD should be favored to obtain a more accurate identification. Plumbonacrite may be more widely present in historical paintings, but inefficiently detected with spectroscopic techniques. It shows as well that the different lead carbonates phases were found in protrusions over time. However, the limited statistics prevent us from generalizing our conclusions to a broader trend over the full model painting and the analysis of many protrusions would be necessary to draw any conclusion about a systematic transformation of one lead phase into another.

Coming back to the “Walnut oil – litharge” system shown in Fig. 6, the precise analysis of lead hydroxyl/oxy/carbonates shows the absence of any peak at  $1045\text{ cm}^{-1}$  which suggests the presence of plumbonacrite, instead of hydrocerussite as previously hypothesized.

#### Can lead driers be identified in historical paintings? [Subheading]

From the previous example, it is noteworthy that no PbO (being litharge or massicot) was detected in the painting, demonstrating that this phase is instable in the tested conditions, and confirming the fact that assessing its use in historical paintings is extremely difficult (Higgitt & Plater, 2004, White & Kirby, 1994). Conversely to the pigments which are at least partially stable and identifiable through their elemental or phase composition, determining if PbO was used in a painting is a real challenge. Similarly, while its use can be hypothesized based on historical texts, the analytical determination of lead acetate is extremely difficult (Keune, 2005).

Different methods have been proposed to assess the presence of lead driers: i) a macroscopic low Pb content (e.g. detected by XRF) and the absence of lead pigments as observed in a corpus of Picasso paintings in Antibes (Casadio, *et al.*, 2013), ii) a microscopic diffuse presence of lead in the matrix (and not concentrated in specific grains), as observed in intermediate/ isolation layer of the *Sherborne Triptych* (late 15<sup>th</sup> C.), *The Descent from the Cross* by Rogier van der Weyden (1399-1464) and the *Triumph of Death and the last Judgement*, attributed to Hermann Tom Ring (1521-1596) (Ferreira, *et al.*, 2008), in the *Descente des vaches* (1834–1835) painted by Théodore Rousseau (Keune, *et al.*, 2013) as well as in 102 of the 155 colored ground layers analyzed by Duval in French paintings dated from the 17<sup>th</sup> and 18<sup>th</sup> C. (Duval, 1992).

In an extensive study of grounds from 103 paintings executed in Paris, the Lorraine duchy, Italy and Flanders between 1600-1640, E. Martin established a classification of grounds, based on their color and composition (Martin, 2008). She proposes to identify additives as siccatives if they represent less than 20% of the mixture, as a secondary component above this limit, and as a main component above 50%. With this classification, lead white is identified as the main component in 7 paintings (mainly Italian) and lead white and minium are identified as drying agent in 65 and 10 paintings

respectively, showing a very common use of such siccatives in Europe at this period. It has to be noted that lead white and minium are hypothesized based on visible and electron microscopy (basically color and presence of lead). Other forms of lead cannot be excluded. *“The small amount of diffused lead that can be introduced from other lead-based compounds during oil preparation is impossible to distinguish from lead due to lead white, and is not considered here”*. In light of the observations discussed in this paper, it would be extremely important to revisit all these occurrences of under-considered diffuse-lead and to track more precisely the presence of lead soaps and the different lead-containing phases, using  $\mu$ FTIR and  $\mu$ XRD.

Finally, the reproductions presented here focus only on the role of lead driers, and litharge in particular, but it should be noted that many other factors (e.g. external source of fatty acids, climate and storage conditions, water damage, etc.) can influence the formation and evolution of metal soaps in paintings and deserve a similar attention.

## Conclusions [Heading]

In summary, there has been an extensive effort in reviewing the presence of metal soaps in paintings. The origins of metal soaps in paints can be many: they can be introduced as such, as in modern paintings. Many historical texts also provide recipes for *in-situ* synthesis of lead soaps in lead-based media. Besides, they can also form at a longer term, in particular during the drying process, and potentially stabilize the paint network. Accordingly, as discussed here, identifying i) if metal soaps were produced on purpose by the painters and ii) if they were introduced as such in the paint or appeared later and iii) which metal compounds are responsible for the saponification, are very complicated questions due to the short, mid and long term chemical and physical evolutions which modify paint composition and structure. All hypotheses should be considered, in particular in the case of early (<1850) paintings.

The impacts of metal soaps in paints are also many: metal soaps can be used by the painters or paint manufacturers to master the physical properties of paints during application or during drying, metal soaps can also be responsible for degradations (protrusions, efflorescences, etc.). The interface between friend and foe is extremely delicate. Regarding degradation phenomena associated to metal soaps, it is important to check if metal soaps and other associated metal compounds are indeed concentrated (or absent) in degraded area. Imaging micro-analytical techniques are essential in this respect. The fundamental concern is probably more the metal soap concentration and (re)mobilization than merely their presence (Boon, *et al.*, 2006).

The historical recipes of lead-oil media report complex multi-steps processes (mixing, introduction of water, heating...). It is very important to note that these different steps, their duration, the proportion and quality of ingredients, the temperature, will have fundamental effects on the kinetics of oil saponification, and accordingly on the ester/soap ratio in the final paste. It is also a clear demonstration that unfortunately it seems impossible to retroactively determine the initial proportion ester/lead soap based on i) historical recipes or ii) the present ratio. Indeed, the same basic recipe can end into various compositions depending on the operator (the control of quantities, of coarseness of powders, duration, temperature, decantation, filtration, when done by the artists were not necessarily as accurate and reproducible as a chemist would achieve today). Moreover, this saponification reaction can continue for a while, once the paint is applied on support.

In a more generic way, we would like to insist on the following points:

- The ingredients detected today on paintings were not necessarily introduced by the painter (e.g. pentalead tricarbonat dihydroxide oxide in our model paint),
- Conversely, the ingredients originally used by the painter may be completely absent today in the paintings (e.g. litharge in our model paint),
- the metal soaps detected today do not necessarily result from long term alteration or degradation, but can be synthesized in less than one hour, conscientiously and on purpose by the painter,
- based on the many historical recipes, the role of lead driers, litharge in particular, in the formation of lead soaps is essential.

### Acknowledgements [Heading]

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