

REVIEW

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But aren't all soaps metal soaps? A review of applications, physico-chemical properties of metal soaps and their occurrence in cultural heritage studies

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Abstract

Metal soaps, the organic salts resulting from the interaction of fatty acids and metal cations, arouse interest in the scientific field because of their versatility in a great range of chemical applications as well as because of the mechanism of their formation during degradation processes. This article presents a review of the synthetic pathways used to produce metal soaps, their relevant physico-chemical properties, and how these reflect in their applications. Common industrial uses of metal soaps are reported, with a particular focus on those applications, such as cosmetics, paints, and coatings, that have an impact on the cultural heritage field. In addition, the occurrence of metal soaps in cultural heritage studies is presented, ranging from archaeological and ethnographic artefacts to fine art objects, and discussed per class of materials. An overview of the presence or absence of metal soaps in historical artefacts due to the interaction of metal parts or mineral pigments with fatty acids is given herein. This collection shows a variety of situations in which metal soaps—particularly lead, zinc and copper soaps—can form on composite objects made of different materials such as wood, leather and fatty-acid-containing materials (e.g., waxes), in the presence of metal, metal alloys or pigments.

Keywords Metal soaps, Metal carboxylates, Painted artworks, Degradation

Introduction

In its fundamental definition, an organic salt of a metal cation and a carboxylate anion containing at least eight carbon atoms in the alkyl chain is called a soap [1]. However, in the common acceptance of the term, only the alkaline salts—those of soda and potash—and the ones of ammonia are regarded as soaps [2]. Even so, many soaps

are made from other metals, typically heavy-metal cations, and they differ from alkaline soaps because of their water insolubility and increased solubility in non-polar solvents [3]. They are referred to as metal soaps—a term that was used as early as the second half of the 18th century [4]—to distinguish them from ordinary alkaline-metal soaps, and they have been employed in various applications based on their chemical properties. Twenty-seven metals, including zinc (Zn), lead (Pb), copper (Cu), and aluminium (Al), in combination with common fatty acids such as stearic, palmitic, oleic, linoleic, as well as less mentioned ones such as naphthenic, tall-oil, and rosin acids, have been reported to form metal soaps [3]. However, in the field of cultural heritage, metal soaps are identified as the metal complexes with saturated mono and di-carboxylic fatty acids [5].

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This article aims to provide a review of the knowledge concerning metal soaps, maintaining a dual perspective: the physico-chemical aspects of this class of compounds and their industrial uses are presented from a chemical standpoint through a collection of both fundamental and application-based publications on the topic; at the same time, these aspects are put in relationship with metal soap formation as a chemical phenomenon observed in heritage studies. By doing so, we aim to provide more general chemical knowledge to cultural heritage professionals who would like to approach metal soap studies on objects of cultural patrimony. The commentary on the formation of metal soaps on a selection of supports used in the history of art beyond the most-known canvas will instead allow pure and applied scientists to examine fundamental chemistry concepts in the context of heritage conservation studies.

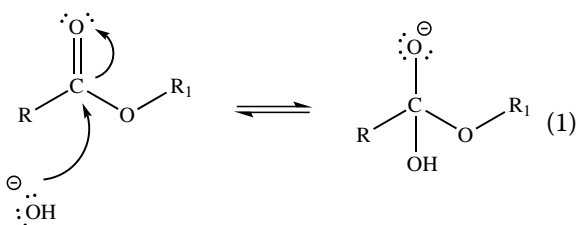
This review paper is set in the framework of a research work on the formation of metal soaps on painted metals. For this reason, particular attention is given to those metal cations that are also of interest as supports and that are commonly less investigated in metal soap studies (e.g., copper). It is organized into two main sections. The first section illustrates aspects related to the production of metal soaps, their physico-chemical properties and their uses, with particular attention to the paint industry. The second section targets cultural heritage studies and discusses the occurrence of metal soaps due to the pigment-binder interaction on traditional paintings and between fatty-acids-susceptible and fatty-acid-containing materials.

Physico-chemical characteristics of metal soaps and their uses

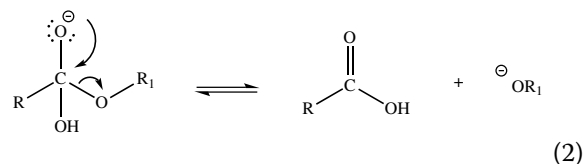
Production of soaps and metal soaps

Saponification is the alkaline hydrolysis of fatty acid esters that results in the formation of the metal salt of a fatty acid. The general reaction mechanism, which is catalysed by a strong acid or base, consists of three main steps. In the following reactions, we provide an example of such a mechanism for alkaline-catalysed hydrolysis [6]:

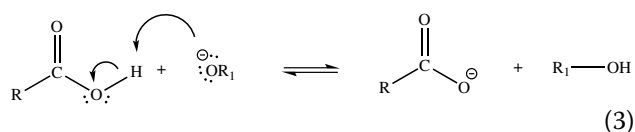
- 1 Nucleophilic attack on the carbonyl group of the ester by the hydroxide anion, with the production of the orthoester (1);



- 2 Leaving group removal, and generation of the carboxylic acid and the alkoxide (2);

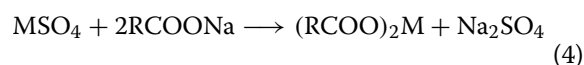


- 3 Deprotonation of the carboxylic acid by the alkoxide ion (strong base) and production of the carboxylate ion and the alcohol (3).



Alternatively, the soap industry also utilises the neutralisation method, i.e., a reaction where the carboxylic acid is neutralised in the presence of a base to synthesise metal soaps derived from magnesium, transition metals, and aluminium. This method is ideal for the selective production of single fatty acids soaps. Moreover, this is a required synthetic step in producing soaps with controlled physico-chemical characteristics [3, 7].

Soaps of heavy metals are prepared through two main methods of synthesis, i.e., precipitation and fusion [3, 7]. The first method is a double decomposition reaction (metathesis), where an aqueous-alcoholic solution of a soluble salt (typically sulphates, nitrates, or chlorides of a metal (M being any metal considered)) is made to react with a soluble alkali salt of the fatty acid (4) [2, 3, 8]. This reaction which transforms a soap into another soap, is also called “trans-saponification” as an adaptation of the “trans-esterification” mechanism [9]. The metal soaps made following this process appear as a highly hydrated precipitate at the bottom of the solution.

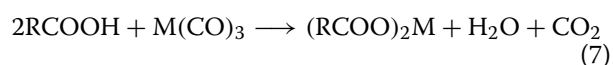
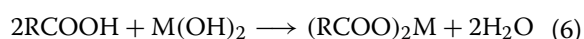


In a work by Corbeil and Robinet aimed to characterize the metal soaps found in paint films, this two-step precipitation method was used to synthesise soaps of zinc, lead, and copper cations [10]. However, only the oleate of zinc, lead and copper ions, and zinc linoleate were obtained as solid crystalline salts; the other combinations of oleic and linoleic salts with zinc, lead, and copper cations resulted in amorphous agglomerates. Other studies have reported poor crystallinity of synthetic metal soaps depending on the solvent in which the reaction occurs [3].

In the fusion method, the carboxylic acid and the oxides, hydroxides [11] and salts of the desired metal, e.g., carbonates [3], nitrates [2, 12], and acetates [13] are made to react directly at temperatures between 180 and 300 °C [3]. By

using this method, Yu et al. produced iron (III) oleate as precursors of iron oxide nanoparticles [11]. A description of the general reaction is provided below, using oxides, hydroxides, and carbonates as reagents [5–7].

Since the 1950s, several patents were granted that describe the synthetic pathways for the manufacture of metal soaps (e.g., U.S. Pat. No. 2650932 [14], U.S. Pat. No. 2890232 [15], U.S. Pat. No. 2945051 [16], U.S. Pat. No. 3803188 [17], and U.S. Pat. No. 4316852 [18]).



Other synthesis strategies include electrochemical methods. Scientific literature primarily refers to the synthesis of copper carboxylates through electrochemical procedures [19, 20]. These methods are employed because they present several advantages concerning reaction selectivity, rate control and the possibility of having a “reagent-free” reaction [19]. The reaction occurs in the organic phase between carboxylic acids and Cu(II) ions generated in the aqueous phase solution from the corroded anode in the presence of chlorides [20]. Similarly to the traditional chemical methods, electrochemical reactions can also be multi-step, where an alkaline metal soap is first produced and then made to react with the copper corrosion products formed locally at the anode [20]. According to Carvalho, by using this method from palmitates as precursors, a pure compound could not be obtained, but rather a mixture of copper palmitate ($\text{C}_{64}\text{H}_{128}\text{Cu}_2\text{O}_8$), cuprite (Cu_2O) and atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$), due to the presence of chlorides in the electrolytic cell to increase the conductivity of the electrolyte [20]. The proposed anodic and cathodic reactions for this process, which is inspired by the production of verdigris pigment, are published in [20].

Chemical synthesis procedures are generally more common than electrochemical methods, which are mostly found in association with laboratory research purposes.

The mechanism of formation of metal soaps in oil paintings is briefly described in the following paragraphs.

Properties of metal soaps

Physico-chemical properties of metal soaps are strongly related to their structure and the nature of the metal.

For intentionally synthesised metal soaps, colour is dictated by the electronic configuration of the cation, resulting in a similar colouration to the one of their most common salts. Nickel and copper soaps will therefore be expected to assume green colouration; saponification of lead, zinc, aluminium and alkaline metals will result in white soaps, manganese soaps will be lavender in colour, and iron soaps show red-to-brown hues [2, 3, 9]. When colour properties of synthetic soaps are compared to those found in paintings, differences have been reported, according to which metal soaps manifest themselves in various ways, including darkening, efflorescent crusts, and crystalline exudates, leading to increased transparency [4, 21, 22].

Due to the difficulties in obtaining such compounds in the purest form, melting points are not uniquely defined, and a range of temperatures is instead provided [3]. Nevertheless, the melting point of different metal soaps showed trends that can be related to the characteristics of the cations [9]. In a dedicated study, Sutrisno and co-authors demonstrated that the synthesis and characterisation of Zn, Al, and Mg soaps from sunflower oil showed inverse proportionality between melting points and ionic character, or, in other words, a positive correlation between the metal soap melting point values and the covalent character of the corresponding cation–anion bond [9]. The ionic character of a bond is determined by the polarisation of the ions, which is a combination of the ionic radius and the effective nuclear charge. In practical terms, ions having a smaller ionic radius and a higher charge will be more prone to polarise the bond strongly. The result of this is that Zn^{2+} ions, that have a greater nuclear charge than K^+ , Mg^{2+} and Al^{3+} , even though they have a larger ionic radius, will be more capable of polarising carboxylate anions than other cations [9].

Along with the decrease and increase in melting point, other properties of the carboxylate compounds are affected by the presence or absence of polarisation. For instance, when the covalent character of the bond increases, the solubility of the soap in polar solvents will reduce, and the corresponding infrared spectra will show a shift in the carboxylate stretching vibrations (νCOO^-) [9]. A shift towards higher frequency will be noticed for the COO^- antisymmetric stretching band, whilst the symmetric band will be found at a lower frequency [23].

In their powder form, metal soaps are highly hydrophobic; however, their crystalline presence in traditional paintings has been associated with increased hygroscopicity of the painting’s surface [24]. As far as the solubility of synthetic soaps goes, Bossert [3] reported their poor solubility in water and increased solubility in organic

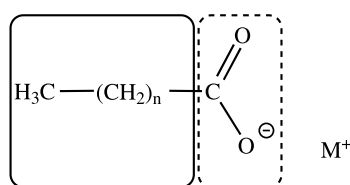


Fig. 1 The hydrophobic–hydrophilic double nature of metal carboxylates. The full and dotted lines highlight the hydrophobic alkyl radical and the carboxylate group, respectively

solvents [25, 26]. In a work by Sutrisno et al., it was found that the synthesised zinc and aluminium soaps are soluble in chloroform and insoluble in n-hexane and methanol [9]. Additionally, heavy-metal carboxylates possess a combination of polar functionalities and non-polar molecular regions within the same molecule ([3], see Fig. 1). This property, which can be quantified by hydrophilic-lipophilic balance (HLB) values in the range 13–16 [27, 28], determines most of their applications exploiting the alkyl chain's hydrophobicity and the metal cation's catalytic action. Table S1 (supplementary materials) provides a summary of the properties of different soaps. It is crucial to point out once more that not all metal soaps listed in the table can be found within paint layers of traditional paintings. Current research has highlighted how fatty acids involved in metal soap formation within paint layers are almost exclusively saturated—palmitic and stearic, or associated with the presence of dicarboxylic azelaic acid or occasionally by monounsaturated oleic acid [5]. The availability of such fatty acids is directly related to the presence and stability of an ionomeric network within the structure of a polymerised drying oil (see also [Metal soaps in cultural heritage](#)). Palmitic, stearic, and azelaic acids are the three free-form saturated acids mainly present in polymerised oil paint. For what concerns palmitic and stearic acid, their position within the triglyceride promotes their hydrolysis, with 1 and 3 favoured [29]; azelaic acid is instead the degradation product resulting from oxidative reactions of unsaturated C18 fatty acids [30].

Uses of metal soaps

As previously mentioned, the hydrophobic-hydrophilic nature of the two extremities of the metal carboxylate molecules allows for a wide range of applications. They can be utilised as emulsifiers for water-in-oil (W/O) emulsions. For this reason, they are often found in cosmetics and lubricants as additives.

Besides their colloidal and surface-active properties, they are also used in cosmetic and pharmaceutical applications for their antibacterial properties (copper soaps) or excipients. Cosmetic and pharmaceutical properties of lead oleate have been known since antiquity, as reported

by the Greek physician, pharmacologist, and botanist Dioscorides in the *De materia medica* (1st century AD) [2]. Evidence of the presence of lead palmitate in cosmetic products was also found in Ancient Egyptian (18th dynasty) containers preserved at the Louvre Museum, possibly being a degradation product from lead-based compounds added to the ancient formulation [31]. In contemporary times, some countries have authorised sodium stearates in creams, lotions, animal food, and packaging ^{1,2,3}. In cosmetics, sodium and zinc stearates are added as a lubricant and thickening agent to improve texture; aluminium, magnesium, calcium and zinc stearate are used as pharmaceutical excipients in the manufacture of ointments, powders, and tablets ⁴.

In the plastics industry, metal soaps are widely used in the manufacture of PVC products and during the processing of numerous polymers, including polyamide, polyethylene, polypropylene, ABS, and fibre-reinforced plastics (e.g., sheet moulding compound and bulk moulding compound). In addition, calcium stearate, barium stearate, and their laurates, used as internal lubricants in PVC formulations, also act as co-stabilisers that increase the heat stability of plastics. Other examples include mixed calcium/zinc soaps, which are used as a heat stabiliser for PVC [32]. Among zinc soaps that are used as external lubricants in PVC formulations, zinc stearate and zinc laurate also have a reducing effect on the initial colouring [33]. Zinc soaps also have catalytic properties and are used as colour binders or activators in rubber vulcanisation [34, 35].

The hydrophobicity of metal soaps is exploited in the building industry, where they are added as water-resistant agents. Additionally, they are used as surcharge and lubricating agents in a variety of applications in the pencil, grease, metal, and paper industries. In the latter, metal soaps also serve as chelating agents for pigments [3].

A relevant field of application is that of the paint industry, where metal soaps are added to the paint to obtain matte and abrasive coatings and to accelerate the drying process of the industrial formulations, which principles

¹ Food Additives Permitted for Direct Addition to Food for Human Consumption - Gums, Chewing Gum Bases and Related Substances. (Mar. 29, 2022). 21CFR172.615.

² Food Additives Permitted for Direct Addition to Food for Human Consumption - Multipurpose Additives. (Mar. 29, 2022). 21CFR172.863.

³ Food Additives Permitted in Feed and Drinking Water of Animals - Food Additive Listing. (Mar. 29, 2022). 21CFR573.280.

⁴ Final Report of the Safety Assessment of Lithium Stearate, Aluminum Distearate, Aluminum Stearate, Aluminum Tristearate, Ammonium Stearate, Calcium Stearate, Magnesium Stearate, Potassium Stearate, Sodium Stearate, and Zinc Stearate (1990). *Journal of the American College of Toxicology*, 1(2): 143–177. doi: <https://doi.org/10.3109/1091581820901315210.3109/10915818209013152>.

will be deepened in the dedicated section hereafter. An overview of industrial uses of metal soaps can be found in the supplementary materials to this publication and in [3].

Metal soaps as oil paint siccatives

The use of metal soaps as siccatives—also called drying agents or driers - that act as catalysers in the polymerisation reaction of oil paints is particularly relevant for art conservation.

Driers can be grouped into three categories:

- primary driers, also called active or oxidation driers,
- secondary driers, also known as through-driers,
- auxiliary driers.

Primary driers are autoxidation catalysts that act when the surface dioxygen concentration is the highest. Autoxidation catalysis depends on the two accessible valence states of the metal drier to perform hydroperoxide decomposition. Cobalt is the most widely used metal in primary driers. Its advantages reside in effectiveness at room temperature and compatibility with a broad range of coatings and varnishes. However, cobalt soaps have been reported to incur deactivation problems, or the so-called “loss of dry”, through the formation of insoluble cobalt(III) hydroxides [36]. Loss of dry occurs in pigment-containing paints upon ageing, where the drying times stretch and become ineffective after a particular storage time. The reason for this phenomenon can be identified in the failure of the drier’s action due to surface adsorption, hydrolysis (especially for waterborne paints), and, like in the case of cobalt driers, the formation of insoluble compounds of the drier metal [36]. For this reason, most researchers are investigating the possibility of replacing cobalt in the design of new driers. In a few studies, manganese was examined as a substitute for cobalt [37, 38].

Manganese soaps were already used as primary driers, often in combination with cobalt soaps. The addition of amine ligands was found to enhance the autoxidation activity of manganese soaps significantly. However, a disadvantage of using manganese is the brown colour of its compounds in trivalent state, which makes them not compatible for applications to light coloured or white paints [37, 38].

Iron complexes are known for their redox catalytic properties in aqueous solutions. However, in non-polar solvents and at room temperature, they are not good drier catalysts since Fe(III) ions are not easily reduced [39]. This behaviour impedes the redox cycle necessary for catalytic hydroperoxide decomposition. Moreover, like manganese soaps, iron complexes are intensely coloured, narrowing their application possibilities [39].

As a general practice, primary driers are used only in co-presence with a secondary or auxiliary drier [39].

Secondary driers are responsible for the cross-linking of the paint layer. Lead has traditionally been used as a secondary drier. After its ban worldwide, zirconium has been widely accepted as its replacement [40, 41]. Alkyd paints have been reported to dry quicker with a combination of bismuth soaps and cobalt driers. Barium, strontium, and aluminium are other known alternatives to lead-based driers. However, the latter can cause embrittlement of the paint layers [39].

As their name suggests, *auxiliary driers* are used in combination with other driers, i.e., primary driers, to enhance their activity. Their molecular mechanism of action is not known—some of them are only known for retarding the action of the primary drier—but they have visible positive effects on the overall quality of the paint film. Calcium is one of the most used auxiliary driers. It improves the hardness and gloss of the paint films, also under harsh environmental conditions [39]. Zinc, lithium, and potassium driers are used in combination with cobalt driers in paint films, where they help regulate the overall drying rate, hence inhibiting the wrinkling of the paint film [39]. Driers are often used in combination to increase viscosity rate change in the paint film. Frequently used drier combinations are, for example, Co/Zr/Ca, Co/Pb/Ca, or Mn/Zr/Ca [39].

Cobalt, manganese, iron, and lead soaps have been ubiquitously added to modern paint formulations to promote the oxidation and cross-linking of unsaturated oils. In the 1990s, when metal soap investigation developed in the cultural heritage field [4], some studies focused on the history of siccativ compounds for oil formulations.

According to a comprehensive work by Carlyle on driers in 19th-century Britain, during this period, the oxidative mechanisms through uptake of oxygen from the oil medium were understood, and driers were defined as agents that would catalyse the process of curing of the oil [42]. Until the 1860s, these were mainly metal compounds and their pigments, often based on lead, zinc, and occasionally, copper in the form of verdigris. However, after this period, and especially after the 1890s, British oil painting manuals started mentioning the use of manganese-based compounds as driers. Historical sources hint that cobalt driers were also known, but they do not appear in catalogues or handbooks of the time [42].

Litharge, white lead, and red lead were the lead-based driers used in the preparation of drying oil during the 19th century. However, until the 1890s, lead acetate was the only lead drier available in 19th-century artists’ colourmen catalogues. Scott Taylor reported in 1890 that lead pigments and compounds, especially those containing at least 30% lead hydroxide, would be chemically

active, which would be detrimental to the oil and other pigmented oil formulations [42]. The role of lead soaps as driers was only mentioned in the early 1970s [42].

However, it is important to notice how compounds like lead white and lead red that are often found in association with lead soaps were contextually used as pigments [43]. Minium was also hypothesised to have been added intentionally as paint drier, other than being used as a pigment, and it has often been found in correspondence with protrusions in oil paintings [43]. In their analysis of a collection of traditional recipes, Cotte et al. have identified several instances in which the artists purposefully utilised the reaction of lead compounds with oil to synthesise metal soaps locally as driers. These traditional processes also involved the heating of the lead compounds-oil mixture and, during the 18th and 19th century, the introduction of water in the preparation to control temperature and avoid the burning of the oil. These variables affect their physical characteristics, such as the colour of the resulting medium and its rate of saponification [43]. This double use of lead compounds as driers and pigments makes it non-trivial to understand whether encountering lead soaps is a sign of degradation or a part of the original composition of the painting. This is especially true when the compounds used are not sufficiently stable to be detected in the paintings together with their soaps, like in the case of litharge, massicot and lead acetate [43].

According to Carlyle [42], zinc-based compounds were deployed as drier *de facto* throughout the 19th century; manganese was introduced later as a replacement for lead [42]. In a recent study, Garrappa et al. have detected zinc stearate as dispersing agent in late 19th-early 20th century tube paints [44]. However, the tendency of added metal stearates to modern formulations in forming aggregates that can be dangerous for the appearance and stability of the painting surface is still poorly investigated.

In the early 1920s, metal naphthenates became the first modern driers to be developed for the purpose [39]. The most recent siccatives are based on synthetic acids, such as 2-ethyl hexanoic acid and versatic acid. Due to their branched structure, these have the advantage of being highly soluble in apolar mediums like the oil-binder system [39].

Metal soaps in cultural heritage

Besides their intentional presence as dryers in modern formulations, metal soaps also form naturally as the result of a saponification reaction that occurs in fatty-acids-rich materials when the organic component is in intimate contact with a source of metal ions.

Numerous composite objects exist where metal ions are provided by a metal substrate or by a core element

of mineral pigments. In the same way, the reactive fatty acids can be present within many organic elements of the object, such as treated wood, textile, and leather, or as breakdown products of lipid-containing organic remains in archaeological findings [20, 45]. In traditional paintings, the metal ions are only provided by the mineral pigments. In contrast, the fatty acids are contained in the binder both in its original composition and as the result of its degradation. For this reason, metal soap occurrence has been reported not only in oil paintings, where they are widely identified and studied [13, 46–55], but also in a proteinaceous binder (egg yolk-based tempera paintings), where lead soaps were found in correspondence with pale yellow paint layer consisting mainly of lead-tin yellow type I [56]. As the name suggests, oil paintings rely on the use of oils, particularly drying oils such as linseed, poppyseed, and walnut oil, as a medium in which the pigment is dispersed. From a chemical point of view, drying oils are triglycerides of unsaturated and polyunsaturated fatty acids, containing carbon-carbon double bonds in the aliphatic chains. Oleic acid (C18:1), linoleic acid (C18:2) and linolenic acid (C18:3) are the main fatty acids in triacylglycerides of linseed oil [57]. Known for solidifying at room temperature, this class of oils dry—or cure—to a tough, solid film after exposure to air at room temperature. The hardening mechanism has been widely investigated in the past decades [58–61]. It is a multi-step process involving metal-catalysed radical autoxidation, i.e., the reaction between atmospheric oxygen and unsaturated C-C double bonds [62], followed by polymerisation and cross-linking to a molecular network [63]. This way, high molecular weight polymers suitable for film formation are produced from low molecular weight unsaturated triglycerides.

Already during the curing of the oil, several degradation reactions take place. Radical reactions occur due to the presence of peroxide species, which give rise to secondary and tertiary products, i.e., epoxy, hydroxyl, oxo and carbonyl moieties [22, 46, 62, 64]. In linseed oil-based binders, the autoxidation process, which implies autoxidation of allylic moieties of the fatty acids' side chains, allows the formation of a cross-linked structure—the polymer network—through ether and peroxy-bonds [46]. Higher oxidation products also form over time, resulting in aldehydes and carboxylic groups. Spontaneous hydrolysis of the ester bonds also occurs with the production of additional free saturated fatty acids. These isolated fatty acid molecules can later react with metal ions, resulting in metal soaps [5]. Metal soaps are consequently complex degradation products [55]. Parallel to the process of hydrolysis, carboxylates are formed within the polymeric network due to oxidation. In detail, given the mobility of polymer segments to ensure the proximity

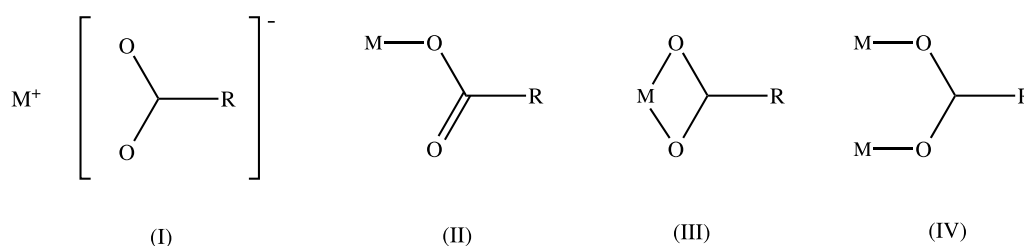


Fig. 2 Chemical structures of metal carboxylates (adapted from [45, 65])

of carboxylic groups, metal ions can transfer from adjacent ones. This mechanism progresses until many of the free carboxylate groups are bound to metal ions, therefore forming an ionomeric-like polymer network [5, 55]. This process has been shown to increase the stability of the oil binder, since divalent ions will coordinate two carboxylate groups and create additional cross-linking in the polymer chain. Hydrolysis due to the presence of water molecules degrades paint layers as it negatively affects the stability of the ionomer polymeric network. Specifically, hydrolysis reactions concern a significant portion of the ester bonds of triacylglycerides in the oil binder. Additionally, when more fatty acids are provided by external sources, e.g., added siccatives, this can also contribute to the formation of metal soaps and further degradation of the paint [5]. Although all these processes are thought to be happening simultaneously, the presence of additives in the formulation can alter the order in which the various phases described occur [5].

Structure of the ligands

In the formation of metal soaps, there are four main chemical structures carboxylates can assume, characterised by different levels of symmetry: (I) ionic or uncoordinated form, (II) unidentate coordination, (III) bidentate chelating coordination and (IV) bridging bidentate coordination [45, 65]. These are illustrated in Fig. 2.

Structures (I) and (III) are characterised by higher symmetry, which gives them characteristic spectral features [45]. These structures and their spectral features are highly influenced by the characteristics of the metal cation (e.g., effective charge, electronegativity), but they are generally insensitive to alkyl chain length. Regarding ions that form metal soaps, some relevant studies showed how zinc, lead, and copper ions are more likely to form metal soaps naturally in the paint film compared to other cations. In 2008, Mazzeo and co-workers showed the pigment-binder interaction between a series of cations and fatty acids within different binders [66]. This work demonstrated that, in accordance with what is known about the reactivity of specific ions towards fatty acids, lead soaps were formed for all lead-based pigments considered, i.e., red lead, litharge, lead white, Naples yellow

and lead-tin yellow. Zinc, manganese, and copper soap formed in both oil and egg tempera paint. Iron soaps were only identified in co-presence with manganese in burnt and raw sienna and burnt and raw umber paint reconstructions [66].

Hereafter, a timely report of current knowledge on the structure of metal soaps formed with ions of interest for this review is provided.

Lead

The degradation of oil paintings due to lead soap formation is probably the most studied phenomenon that involves pigment-binder interaction in the cultural heritage field. Lead soaps are in fact normally observed in association with aesthetically-unpleasant transparency or protrusions that can exert pressure on the paint layers leading to a mechanical expansion, hence, to flaking and cracking of the painting [22]. Driven by a renovated interest in divalent lead coordination chemistry due to lead toxicity and environmental impact, much scientific work has been performed to understand the coordination of the formed carboxylates [47, 67], as well as aspects related to their crystallization, aggregation and migration mechanisms. Solid-state nuclear magnetic resonance studies (ssNMR) helped clarify some aspects of lead coordination in lead palmitate, azelate and stearate [67], showing how the structures formed are similar in the case of lead palmitate and stearate, but they differ from that of lead azelate [67]. Additionally, the impact of the carbon-chain length on the resulting structures was shown and corroborated by X-ray diffraction (XRD) studies [67]. At least five different coordination polyhedra are reported in the literature, with different coordination numbers varying between 2 and 10.24, and depending on whether the $6s^2$ lone pair in the electron configuration of Pb(II) is stereochemically active or inactive [67]. Holo-directed and hemi-directed geometries, where the bonds with ligand atoms are directed towards all the directions of the coordination sphere or describing a hemi-sphere, respectively, are reported in Fig. 3 [67, 68]. These have been identified as typical of high coordination numbers (9 and 10, holo-directed) and low coordination numbers

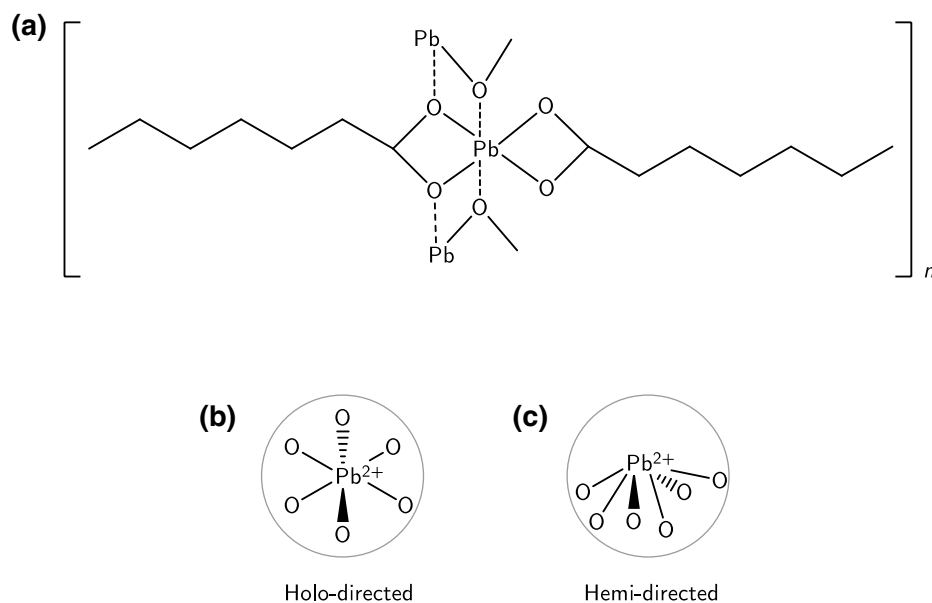


Fig. 3 a General structure of lead heptanoate (adapted from [69]); b, c local environment around Pb(II) for holo- and hemi-directed geometries, respectively (adapted from [67, 68]). The grey circle indicates the coordination sphere

(2–5, hemi-directed). Both types can be instead observed for intermediate coordination numbers (6–8) [48, 67].

The crystallization process of lead palmitate was demonstrated to be a kinetically favoured process with respect to the one of the zinc equivalent, obtained by simply bringing together different lead soap domains within a fully polymerized binding medium [22, 48].

Zinc

Together with lead soaps, zinc soaps are the most synthesised, utilised and found metal carboxylates on oil-painted surfaces. In particular, zinc oxide, the main component of zinc white pigments, is a good adsorption substrate for carboxylic acid functionalities. Several studies have been carried out on the different configurations of zinc carboxylate coordination structures. Four different coordination geometries were identified by Hermans and co-workers [48–50]. In oil paintings, the bonding of zinc oxide to carboxyl groups occurs through dissociative bridging adsorption (Fig. 2-IV and Fig. 4), where carboxyl groups attach to two Zn atoms and the dissociated hydrogen bonds to another Zn atom [70]. The energy of adsorption of carboxyl groups to Zn atoms can be related to increased fatty acid chain length. There are weak Van der Waals interactions between the zinc oxide surface and the carboxylic acids molecules (around 10% of the adsorption energy [71]), whereas van de Waals forces act significantly in lateral chain-chain interactions [70]. Therefore, the adsorption energy decreases with the increasing length of the fatty acid chain [70].

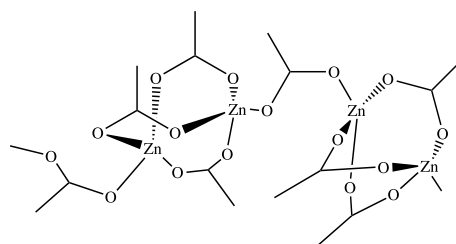


Fig. 4 Zinc oxide-fatty acids polymeric network, showing bridging bidentate coordination (adapted from [70])

As mentioned earlier, in oil paints, once the oil polymeric network is formed and metal-carboxylic group interactions are created, metal cations can migrate and be exchanged between carboxylate groups, forming the so-called ionomer network. This is a cross-linked structure, where ionic groups and metal cations exist and neutralise each other [22, 63]. Formation of ionomeric zinc carboxylate species depends on several factors, such as the pigment content (the highest, the more zinc carboxylates are prone to form) and humidity. Humidity also influences the type of structure adopted, together with the concentration of carboxylate groups, where increased concentration promotes *oxo* fractions over *chain* fractions [72]. Zinc soaps, particularly palmitate, are also found to crystallise at about 121–124 °C, in a multi-step process that involves nucleation, growth and diffusion of metal ions and fatty acids towards metal soaps nuclei. This implies that zinc palmitate is often trapped in an amorphous form within the polymerised linseed oil network [63].

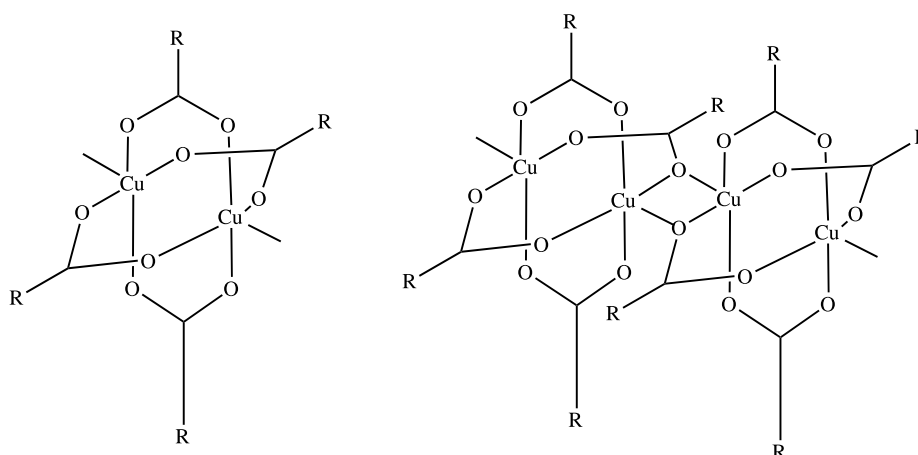


Fig. 5 Structure of paddle-wheel dimer and polymeric network of Cu(II) carboxylates (adapted from [19])

Copper

Copper has been used by humans since the Neolithic, and, through the centuries, copper and bronze metalwork masterpieces have been produced for artistic purposes that we can still admire today [73]. Besides its use in sculpture, copper-based compounds (e.g., malachite or azurite) have been extracted from natural ores to produce green and blue pigments that artists have used for the production of their paintings for centuries [73].

As previously mentioned, due to their interaction with fatty acids, copper ions can form carboxylates as secondary products. Since van Niekerk and Schoening reported copper(II) acetate hydrate in 1953 as the first copper(II) carboxylate dimer, a series of studies on the different structures of copper carboxylates have taken place [19]. Copper(II) can, in fact, coordinate four carboxylate groups from the fatty acids ligands, giving rise to a square pyramidal structure with D_{4h} symmetry. Whether the oxygen of the carboxylate group utilises one or two lone electron pairs to bond to Cu(II) ions, single complexes (paddle-wheel dimers) or polymeric structures can be formed, respectively. In the latter, the carboxylic oxygen is bonded to a copper(II) ion from a second paddle-wheel dimer (Fig. 5) [19].

Aluminium

Soaps of aluminium are seldom addressed in cultural heritage studies, albeit one of the most abundant metallic elements on Earth's crust, that is found in natural minerals like micas, zeolites, or feldspars [74]. Aluminium(III) ions, predominant in aqueous solution, are normally complexed by anionic species in different coordination geometries depending on the pH values. At low pH values, Al(III) complexes assume octahedral geometry

(exa-coordinated); at high pH, tetrahedral coordination is prevalent (tetra-coordinated). In rare cases, trigonal bipyramid (penta-coordinated) coordination geometry is allowed [74]. In octahedral and tetrahedral coordination, the small ionic radius of aluminium ions (0.53 Å for tetrahedral and 0.675 for octahedral) make them strong Lewis acids, hence prone to react with OH^- , F^- , PO_4^{3-} , SO_4^{2-} , but also with organic N- or O-donor ligands (RNH_2 , RO^- , RCOO^-). Aluminium mononuclear and polynuclear carboxylates are typically found in octahedral geometry [74]. In the medical field, they are widely studied to understand the interaction of aluminium with small organic molecules and its role in the development of neurodegenerative diseases [74]. Aluminium soaps are also used in the paint industry as dryers.

Mono- and poly-nuclear motifs are available, where different configurations are obtained, involving sharing edges and corners of Al octa- and tetrahedra [74]. In the 1950s, A.E. Alexander and V.R. Gray concluded that di-soaps were mainly formed from the reaction of alkoxide/fatty acids reaction, as well as from processes in the presence of water (Fig. 6) [75].

Iron

Archaeological evidence shows that iron-based pigmented substances have been in use for several purposes for over 300,000 years of human history [76]. Both +2 and +3 iron oxidation states can result in iron carboxylates. Four possible coordination structures are proposed for iron(III) carboxylates and described in Fig. 7: ionic, unidentate, bidentate and bridging [12].

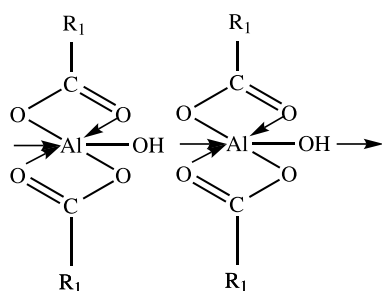


Fig. 6 Structure of aluminium di-soaps (adapted from [75])

Metal soaps occurrence in cultural heritage objects

The scientific literature is rich in studies investigating the formation of metal soaps on different materials, ranging from archaeological objects and decorative art to modern and contemporary artworks. Since the first report of metal soaps in the early 1990s [4, 78], many studies have investigated the saponification reaction between free fatty acids in oil binders and the metal ions from mineral pigments. These studies have targeted pigment–binder interactions [66], crystallisation,

and migration [48, 50, 79–81], and more recently, early-stage formation [82].

Hereafter, an overview of the main classes of cultural heritage objects where metal soaps could be detected is collected and presented to show their ubiquitous nature. Two main categories are identified here:

- archaeological and ethnographic objects, where the metal soaps are formed between a metal and fatty acids-rich components of the functional and utilitarian objects,
- fine arts objects, where oil paint is applied on different supports (e.g., panel, stone, and metal) from different historical contexts and periods.

Archaeological and ethnographic objects

Since the development of a protocol for extracting archaeological organic residues from ceramics between the 1980s and the 1990s, several studies have been carried out aiming to understand dietary habits, agricultural, and ritual practices of past civilisations [83]. In

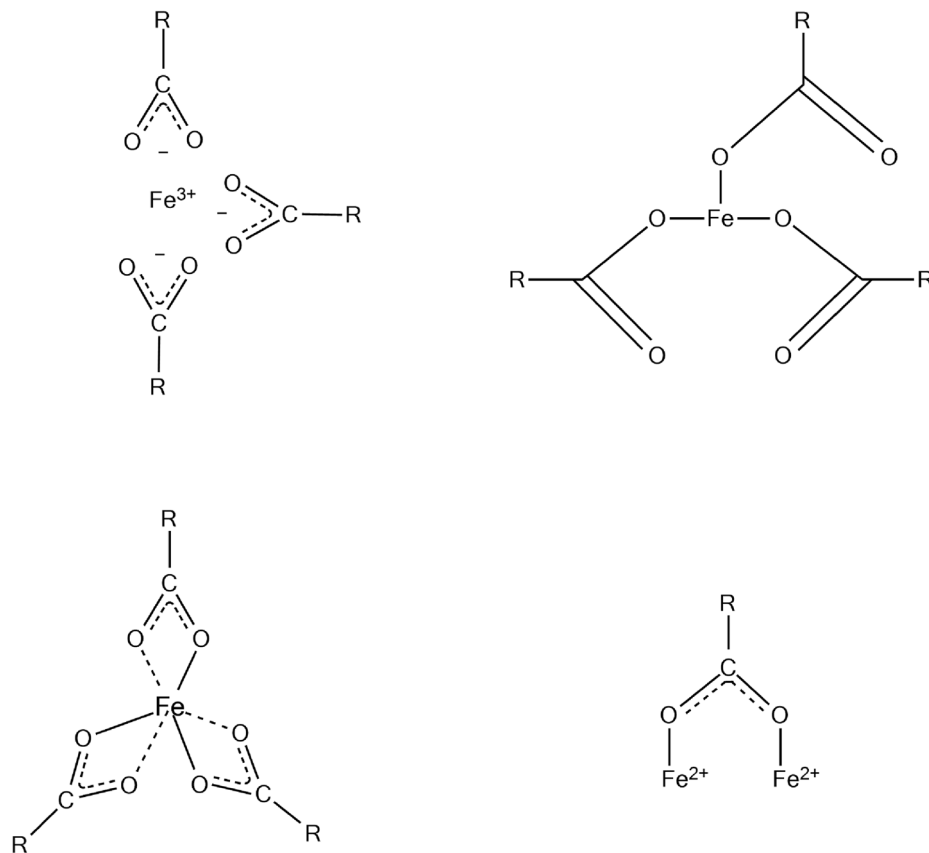


Fig. 7 Coordination structures of iron (III) carboxylates: (from left to right) ionic, unidentate, bidentate and bridging (adapted from [12, 77]). In these representations, the three-dimensional geometry is not considered

2021, a work was published that investigated organic residues in Early Christian Egyptian Metal Vessels of the Byzantine Collection of the Benaki Museum. Here, crystalline metal soaps were found, attributed to the interaction of fatty acids with the metal constituting the vessels. According to the authors, metal soap formation is a favourable chemical process in archaeological contexts, given their tendency to not dissolve in water [84]. In 2022, a multi-analytical approach was proposed to fully characterise copper-organic complexes and organic residues trapped in archaeological copper corrosion [20]. Data from Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, X-ray Photoelectron Spectroscopy (XPS), X-ray Diffraction (XRD), and Mass Spectrometry were presented and discussed, providing a comprehensive analytical characterisation of copper-organic complexes for cultural heritage applications [20].

Ethnographic organic–inorganic composite objects also present degradation phenomena associated with the presence of fatty acids. This can occur due to the interaction between metal parts and organic components, like leather or wood parts [85–87], organic coatings or protective treatments [88]. Leather conservation–restoration protocols, for instance, entail the use of so-called dressings, which consist of oils, fats, waxes, or oil emulsions. Waxy components of most commercial stearic acid-based lubrication or softening products formulated with 50% stearic acid, 45% palmitic acid, and 5% oleic acid tend to migrate through the pores of leather grain and exudate on the surface as bloom [87].

Protective wax coatings were and still are sometimes used in conservation–restoration treatments of metal objects. These protectives can be purchased as commercial formulations or prepared in conservation laboratories and are used as a barrier against moisture and oxygen, contamination due to handling, and as a protective layer [88, 89]. Both the natural colour of the wax and the colouration given through the addition of pigments are exploited in protective waxes to ensure desired aesthetic properties of the object [88]. Pigmented wax-resin infills for paint loss reintegration are still exploited for copper-based artefacts [90].

Copper formate was found on a Benin statue from the National Museum of African Art in correspondence with wax conservation treatments [73, 88]. Pigmented beeswax was also identified in Egyptian antiquities, and copper acetate was associated with its presence [91].

Another example of wax–metal interaction is that of wax statues having a metal–copper–core. A study from 2015 showed that the interaction between the two is likely to induce the formation of metal soaps [92].

Fine arts

Canvas Metal soaps were first associated with oil painting degradation and pigment–binder interaction in the 1990s, when crater-like protrusions, later attributed to the presence of crystalline lead soaps, were identified on the surface of the oil painting on canvas *The Anatomy Lesson of Dr. Nicolaes Tulp* (1632) by Rembrandt, preserved at the Mauritshuis museum (The Hague, The Netherlands) [4]. Since then, much work has been done towards understanding their mechanism of formation within paint layers. Such studies mostly related to the formation of lead and zinc soaps, since these have been reported as the most frequent soaps forming in oil painting [13, 46–55]. A relevant evolution of those studies was the observation that metal soaps form very early in the life of the oil paint, even when they were not initially present as driers, like in the case of modern formulations. For similar reasons, metal soaps are commonly found in modern and contemporary artwork all around the globe. Significant improvements in the non-invasive investigation of metal soaps on contemporary oil paintings were given by a project started at the Georgia O’Keefe museum in Santa Fez (USA) in 2007 when during a routine condition survey, micro-protrusions were identified on the surface of the paintings [93]. The presence of these protrusions on a selection of paintings realised between the years 1924 and 1950 was put in relationship with the type of preparation of the canvas and their ground layers (pre-primed versus prepared by the artist), the pre-primed canvases causing increased vulnerability to the painted surfaces due to formation of lead soaps protrusions [93].

Renowned contemporary art masterpieces have been found to be rich in lead and zinc soaps. Of these, we report a list of the most recent and relevant scientific works for the detection and understanding of their distribution: *The Menaced Assassin* (1927) by René Magritte from the collection of the Museum of Modern Art (MoMA) [94], *Alkemy* (1947) by Jackson Pollock [95], *Chemistry* (1914–16) by Edward Munch at the Munch Aula in Oslo [96], as well as other paintings by Edvard Munch, František Kupka [97], Salustiano Asenso Arozarena, Salvador Abril I Blasco, Enrique Navas Escuriet and José Bellver Delmás (1871–1943) [98], Karel Appel and Asger Jorn (1946–1971), and Argentine concrete art paintings (1940–1960), where zinc soaps were found as additives together with aluminium carboxylates [99]. Other authors have instead based their work on the chemical origins of such reactions, focusing on the water sensitivity of modern oil paintings. It was found that low cross-linking and saponification degree, i.e., the nature of the ionomeric and polymeric network, and high amounts of dicarboxylic acids are responsible for water sensitivity of the 20th century oil paints [100–104]).

Wall paintings Identifying organic materials in wall paintings is often challenging for conservation scientists. In particular, such organic components are typically added in smaller quantities with respect to the inorganic component, i.e., pigments and mortar, and tend to degrade faster than the inorganic materials with which they coexist in the complex wall painting stratigraphy. For this reason, advanced methods of investigation that rely on optimal spatial and spectral resolution, such as those using synchrotron radiation, have been deployed in several studies [105]. It was demonstrated that organic materials were used in wall paintings far more frequently than was previously thought [106–110]. These are primarily polysaccharidic or proteinaceous materials—i.e., vegetable gum exudates, honey, egg, animal glue, milk, and casein—used to confer protection, adhesion, and consolidation to the wall painting. However, oil binders can also be encountered [105, 107, 109, 111]. Due to their consolidating capability, egg-based fixatives or synthetic resins were also used in conservation interventions, somehow contaminating the original composition and making the identification of the original organic components more difficult [110].

When outdoors, wall paintings are exposed to harsh environmental conditions that may affect their preservation. According to the model for organic binders' degradation, the formation of metal carboxylates occurs because of the adjacent presence of mobile free fatty acids and reactive metals from the pigments or ground layers, such as lead, calcium, manganese, copper and zinc, leading to the formation of metal carboxylates. In addition, metal oxalate salts formation is often promoted by metal–oxalic acid interaction and usually occurs at the surface of the mural painting as a thin coloured patina depending on the metal ion (e.g., green for copper) [105, 106]. By definition, metal oxalates do not classify as soaps [1]. However, metal oxalates are organic salts that are often found in paintings on different supports as degradation compounds, and sometimes in co-presence with metal soaps [30]. The origin of oxalic acid is different depending on the composition of the artwork. For instance, some studies have found a relationship between presence of metal oxalates and pigment–varnish interaction [112]; others showed how the formation of metal oxalates is also promoted by the photo-degradation of oils which tend to produce oxalic acid [112, 113]. In previous studies on wall paintings, the presence of oxalic acid has been attributed to the microbiological activity or photo-oxidation of proteinaceous materials, catalysed by Fe(III)-based pigments [105]. Metal carboxylates and oxalates have been identified in several Roman [107], Greek [108], Cypriot [106], and Byzantine [105] wall paintings.

Panel Oil paintings on panel were very common in easel painting practices, especially before canvas came into general use at the end of the 16th century [114, 115]. Metal soaps can be commonly detected on oil paintings on panel in correspondence to zinc and lead pigments [116, 117]. Secondary products from the mineralisation of lead soaps in oil paints, associated with lead red and lead-tin yellow type I in paint cross-sections, have been identified from a Late-Medieval painted wing in the Museum of Cultural History at the University of Oslo [116]. Wood supports are not reported to have a chemical influence on the formation of metal soaps. However, the wood grains' morphology can contribute to generating nucleation centres and preferential directions of formation [118].

Stone, glass and ivory During the 15th century, Italian artist Sebastiano del Piombo (1485–1547) pioneered the creation of paintings on marble, alabaster, lapis lazuli, and amethyst [119]. Such experimentation continued within Europe into the early 18th century. Painting practices on stone are recently gaining popularity, as confirmed by dedicated exhibitions organised in the past few years by Brimo Di Castro Kugel (Manhattan, USA, 2017), the Museo Nacional del Prado (Madrid, Spain, 2018), and the Saint Louis Art Museum (St. Louis, USA, 2022). As oil paintings, these artefacts are also not immune to degradation due to metal soap formation. There is no evidence that the support plays a role in the degradation mechanism. However, metal soaps can be found in the pictorial layers. In a work by Vichi and co-workers, lead soaps, investigated through optical coherence tomography (OCT), were identified on a polychrome carbonate sculpture dated around the 15th–16th century [120].

Similarly, in a recent work aimed to investigate a selection of miniature portraits on ivory, metal and glass supports, lead soaps were detected within the paint layers, both in purely oil-based paints and in those where a mixed technique—indicated as watercolour and utilising a combination of gum and oil—was employed. Interestingly, the typical surface effects due to the presence of lead soaps, i.e., protrusions, efflorescence, darkening, or translucency, were not observed in correspondence with well-crystallised lead soaps [121].

Metal Simultaneously with the development of painting practices on stone, the art of painting on metal also saw its highest expression. This was due to the increasing interest in experimenting with new supports to obtain new virtuous visual effects and challenging the artist's skills and dexterity [122]. Such composite artworks have proven to be much more stable than paintings on canvas with regard to relative humidity and temperature variations [123].

Despite being a neglected field of study, it is worth mentioning the occurrence of metal soaps on some selected exemplars of fine painting on metal or in association with oil coatings on metal technical and industrial objects. A first example is a 17th-century miniature portrait of Italian school, painted on a copper substrate [124]. Here, copper soaps were identified within some green corrosion products that made their way through the paint layer to the surface of the painting [124]. In a second example, two aluminium-based works by Frank Stella, namely *Gobba, zoppa e coltorto* (1985) and *Cricche, crocche e manico d'uncino* (1986), were analysed following the observation of crystalline growths in correspondence with dark red and blue paints [79]. These features were associated with the presence of alizarine crimson oil paint, but not further characterised [79]. Lead soaps were identified in the paint layers of some iron objects belonging to the Conservatoire National des Arts et Métiers (CNAM) collection in Paris in a recent work by Gordon and co-workers [125]. Lead formate was also detected as degradation product on a polychrome lead sculpture from the Oratory Museum, Ouro Preto (Minas Gerais, Brazil) due to the interaction with formaldehyde-containing cleaning products [126].

Technical objects and industrial heritage often consist of copper or iron-based alloys where oil is applied for corrosion inhibition or as a lubricant to ensure the movement of the mechanical parts. When a pigment is added to the coating, metal soaps are often found within the paint layers. However, it is not always possible to identify metal soaps between the metal and the protective layer. The case of iron soaps is particularly interesting, especially since, in the cultural heritage field, there is no mention of the presence of iron carboxylates, except in a few wax statues by Gustave Moreau pigmented with iron oxides⁵. Nevertheless, from a chemical point of view, iron carboxylates exist as stable organometallic complexes that are synthesised for metal-organic frameworks drug delivery systems, water desalination membranes, or as prodegradants to enhance the photodegradability of polypropylene [127, 128]. Additionally, they are encountered on moving components in industrial machinery [129]. For this reason, their formation is widely studied in the framework of tribological studies, which have shown that iron carboxylates can form within layers of lubricants when these are in intimate contact with a metal surface in motion [130, 131]. This is a well-established issue in the tribology field since the formation

of crystalline species is responsible for stiffness and malfunctioning of the mechanism. Iron soaps are believed to form since fatty acids are typically added to lubricants to improve their anti-friction capabilities [132]. However, an excess of such species can induce a reaction with the metal substrate. While in industrial applications, lubricants and corroded parts can be replaced and this might not be perceived as a sensible issue, in industrial heritage studies, where parts often cannot be replaced to maintain the originality and history of the object, this can lead to the poor preservation of the artwork. Additionally, in some cases (e.g., kinetic art objects), the mechanisms and functionality of the artwork must be preserved as part of their artistic life and performance. This adds a layer of complexity to the selection of the correct preservation strategies for the objects in the presence of organic salts [133].

Conclusions

Metal soaps are a versatile class of chemical compounds that are formed when a metal ion reacts with a fatty acid. Due to their unique properties and their ability to act as emulsifiers, lubricants, and surfactants, since the 1940s, metal soaps have been used for a variety of industrial applications in the manufacturing of plastics, pharmaceuticals, cosmetics, automotive, paints, and more. Besides their commercial and technological uses, metal soaps are also found as a degradation product in artworks and machinery, where the metal is in contact with oil-based lubricants and fatty acids. Differences can be highlighted between synthesised metal soaps and those found in cultural heritage artefacts, ranging from optical properties, such as colour, to type of metal soaps formed which depend on the fatty acids available in the oil polymeric network. Therefore, attempting to define metal soaps as an unambiguous class faces constraints due to their dissimilarities and consistent amount of variation.

In the field of cultural heritage, metal soaps are not just found in conventional art media, i.e., oil paintings on canvas, but also in composite objects and less-usual supports, such as wax or metal supports.

The most commonly found metal soaps in cultural heritage objects are those of lead, zinc and copper. In a few instances, iron soaps have also been reported, but not in combination with oil binders in paint media. From the review of the literature on the topic, it is also coming to our attention that metal soaps are not only found in static objects but also dynamic objects (i.e., machinery).

This survey aims to enable chemists to get familiar with the challenges posed by metal soap formation in cultural heritage while providing comprehensive theory about degradation due to metal soap formation to conservator-restorers, conservation scientists and professionals

⁵ Borel, T., Le Hô A.-S., Langlois, J., and Vandenberghe, Y. (2010) Examen et analyse scientifiques des cires de Gustave Moreau. À la recherche d'une chronologie par les examens de laboratoire. From an exhibition catalogue dedicated to Gustave Moreau.

focusing on cultural heritage studies. Although several aspects of the mechanisms of formation, aggregation and migration of metal soaps have been clarified in the past decades, many fascinating angles of the study of this class of materials keep arousing new interest and would surely need further investigation by the scientific community. In this review, we mentioned less common supports or metal ions, and degradation due to motion of metal parts, as scientific questions of interest. Other research angles concern the water and solvent sensitivity of the painting's surface in relation to the presence of metal soaps, a topic that was not elaborated on within this work but could be deepened in future review papers. These aspects have been investigated in recent years [101, 134–136] for their relevance in the decision-making concerning conservation treatments.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s40494-023-00988-3>.

Additional file 1: Table S1. Table of properties of a selection of metal soaps. The table is compiled from [2, 3, 137–142].

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Author contributions

S.R. carried out the bibliographic research and put together the material which contributed to this publication. S.R. wrote the manuscript. L.B., J.B.T. and E.J. reviewed the manuscript and supervised the work.

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Declarations

Competing interests

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