Chapter 14
Taking Different Forms: Metal Soaps in Paintings, Diagnosis of Condition, and Issues for Treatment

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Abstract This chapter introduces a selection of case studies of paintings that present a range of physical manifestations of metal soaps. The phenomena include surface spots, crusts, delamination, and textural features. The role of metal soaps in water-sensitive modern oil paints is introduced. Inferences based on a combination of technical and analytical evidence together with information about the history and context of the works are presented with hypotheses about the causes of metal soap formation or deterioration. Approaches to treatment of the works are introduced in a discussion of aesthetic, ethical, and practical options that address particular phenomena.

Keywords Metal soaps · Crusts · Spots · Delamination · Water sensitive oil paints · Treatment · SEM/EDX · FTIR · Chelating agents · EDTA

14.1 Introduction

The research summarized in this chapter aims to identify a broad range of phenomena related to metal soap degradation in paintings. It draws on evidence gathered from recent studies and inferences from a wide body of published research, comprising fundamental chemical investigations along with case studies that present similar or related metal soap phenomena. Recent advances in knowledge arising from molecular level and model studies of soap formation have informed an understanding of alterations observed in paintings. However, many of the key studies are published in scientific journals that are less accessible to conservators who encounter paintings with deterioration in the studio but may not recognize the range of phenomena. Furthermore, most conservators will not have the resources to undertake chemical analyses that provide specific characterization.

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F. Casadio et al. (eds.), *Metal Soaps in Art*, Cultural Heritage Science,
https://doi.org/10.1007/978-3-319-90617-1_14

Selected examples are presented that exemplify different observed phenomena and highlight questions that might be usefully investigated in future studies. The cases discussed aim to provide a broad classification of manifestations of metal soaps in the paintings or to present instances where commonalities of cause point to the influence of environmental conditions, material composition, or conservation history. The role of metal soaps in water sensitivity of unvarnished oil paintings is also introduced.

The last section of this chapter considers the relevance of research into metal soaps for the treatment of paintings, discussing how an understanding of metal soap-related degradation is important in formulating appropriate treatment approaches. For instance, how such an understanding might impact upon the decision to remove coatings, surface crusts, or fatty acid efflorescence, the cleaning of water-sensitive paints, the consolidation of flaking paint, and the development of suitable preventive measures. Practical approaches to the treatment of deteriorated surfaces caused by metal soap formation are also discussed, alongside ethical considerations.

Different kinds of metal soaps have been identified in paintings and test samples using scanning electron microscopy with elemental analysis (SEM-EDX), Fourier transform infrared spectroscopy (FTIR), and other instrumental analytical methods. While a full review of published studies is beyond the scope of this chapter, key publications that have discussed lead and zinc soap aggregates, crusts, and hazes in paintings include Boon et al. (2002, 2007), Noble et al. (2002), Noble and Boon (2007), Keune and Boon (2007), Jones et al. (2007), Shimadzu et al. (2008), and Van Loon et al. (2012a, b). The five-year PAinT project (2012–2016)[1] sponsored by the Netherlands Organization for Scientific Research (NWO) has advanced our molecular understanding of metal soap formation in oil paint and paintings. Findings from this research project are included in other chapters of this volume.

14.2 Surface Phenomena

14.2.1 Efflorescence and Soap Crusts

The following case studies exemplify different visual manifestations of metal soaps that necessitated the development of specific approaches to treatment; the individual treatment challenges and decisions are detailed below in Sect. 14.5.

Portrait of Carolina Ewen, Circle of Thomas Hudson, c.1750 private collection, oil on canvas

Patches of insoluble white crystals were present on the paint surface of this mid-eighteenth-century British portrait.[2] A sample from the paint surface of an

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[1] http://www.s4a-paint.uva.nl/research-topics/research.html

[2] Report CIA:2215 Department of Conservation & Technology, Courtauld Institute of Art, 2015.

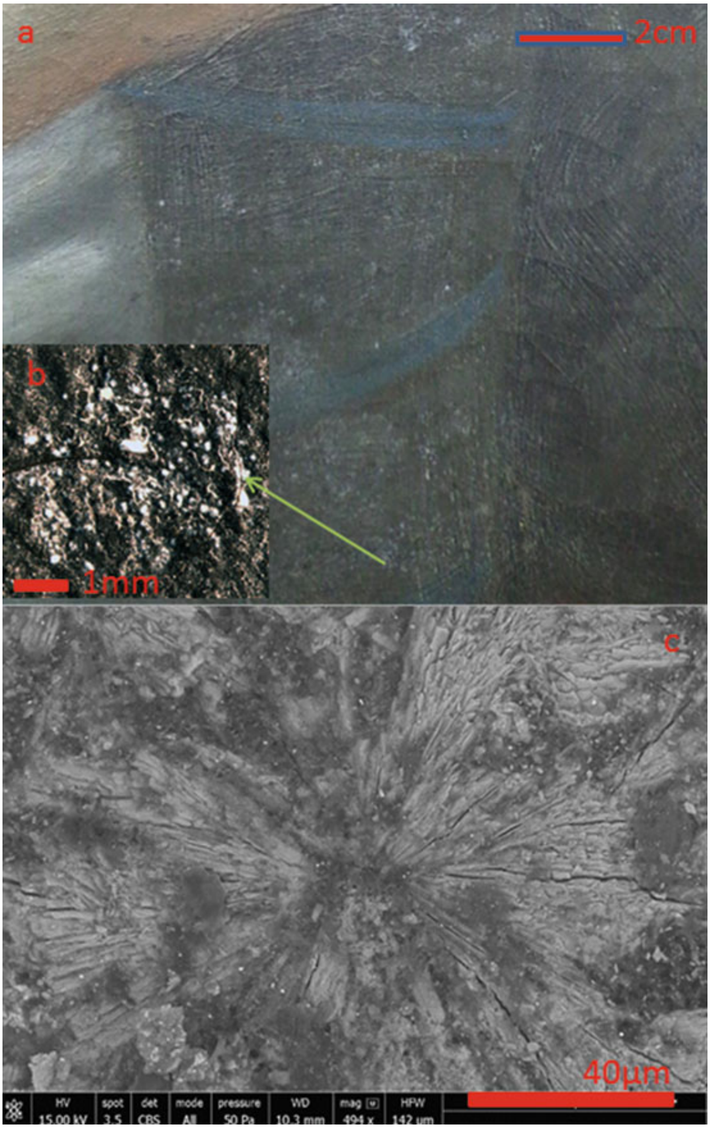

Fig. 14.1 (**a**) Detail of lead soap crystals on the surface of blue drapery in *Portrait of Carolina Ewen*. (**b**) Light microscope image of an aggregate of lead soaps. (**c**) SEM-BE image of the surface of a sample from the same area showing needle-shaped crystals of lead soaps

affected area viewed with SEM in a backscattered election image (BE) and analyzed using EDX showed inclusions of needle-shaped crystals containing elemental lead (Fig. 14.1) FTIR analysis of a surface scraping identified the crystals as lead stearate and re-mineralized lead soaps.

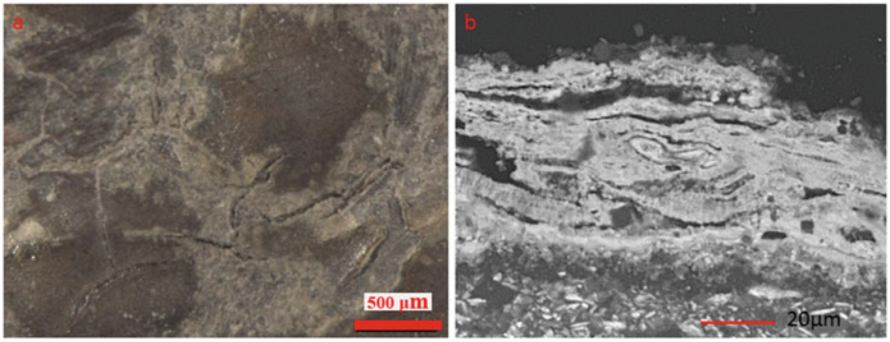

Fig. 14.2 (**a**) Detail from the foreground from *Return from the Front* showing hazy whitish soap crust. (**b**) A cross section from the same area the showing a laminated whitish crust of lead soaps

Return from the Front, Kate Olver, c.1915 private collection, oil on canvas

The foreground of this painting was covered by an uneven, laminated whitish crust of lead soaps with lead sulfate visible in a cross-sectional sample (Fig. 14.2) (Sawicka et al. 2014). The crust is particularly evident in the troughs of the paint following the canvas weave, although in other areas it completely covered the brown painted passages.

14.2.2 Paint-Coating Interactions

Two paintings examined present examples of soap formation associated with paint-coating interaction; the chemical relationship between paint and coating is further examined by Higgs in Chap. 7 in this volume. A third painting, *Female Nude* by Amedeo Modigliani, provided an example in which lead and zinc soaps had formed in the ground and paint in both varnished and unvarnished passages.

Wolmer Wood, Philip A. de László, d.1934 private collection, oil on wood panel

A technical examination of *Wolmer Wood* by Philip A. de László, a Hungarian artist working in Britain, identified the presence of insoluble zinc soaps at the surface of the painting[3] (Burnstock and Van den Berg 2014). The surface had developed a brown discoloration and the composition had become unreadable. Figure 14.3a shows a detail from the top left of the composition before treatment and 3b during removal of the coating. SEM-EDX examination of cross sections and FTIR analysis showed that zinc soaps had formed at the paint surface. These soaps appeared to be caused by the reaction between an oil-containing surface coating

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[3] Report CIA:2093 Department of Conservation & Technology, Courtauld Institute of Art 2010.

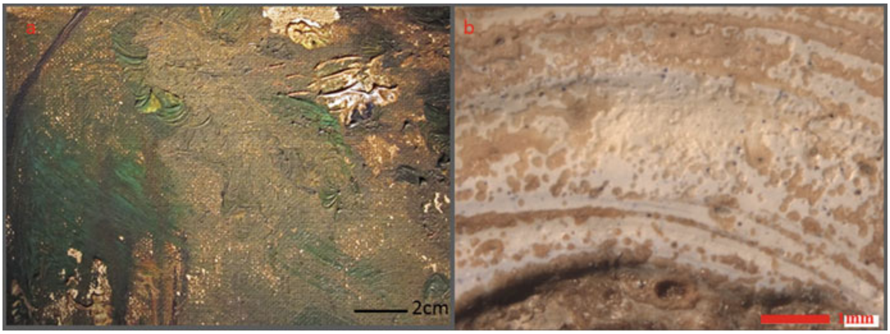

Fig. 14.3 (**a**) Detail of the surface of *Wolmer Wood* before treatment. (**b**) Detail of an area of zinc white-containing paint during removal of the brown layer with zinc soaps, showing pits in the paint surface where zinc soap aggregates have been removed

with zinc oxide-containing passages of paint. Notable in this case is the formation of zinc soap aggregates that are integral both to the insoluble coating and the paint surface. A brown surface residue containing zinc carboxylates was also noted in a painting by Shimadzu et al. (2008).

Cross sections from the painting show the artist's use of zinc white in a mixture with emerald green and cadmium yellow pigments applied over a ground that had been sealed with a protein-containing layer.[4]

Visible and SEM/BE images of a cross section from the zinc soap-containing paint and browned coating (Fig. 14.4a, b) clearly show crystals containing elemental Zn and O at the paint-coating interface (Fig. 14.4c).

In formulating hypotheses on the origin of the now brownish coating, it should be noted that application of an oil-containing varnish over oil paint, or simply applying oil, sometimes referred to as "oiling out," was recommended in artists' treatises in the nineteenth century and was common practice into the following century. If an oil-containing varnish of this sort was used to coat *Wolmer Wood* (whether or not by the artist), then a consequence would be the provision of free fatty acids or possibly acidic degradation products from resin if the applied coating was an oil-resin varnish. These free fatty or resin acids could then react with zinc ions to form soaps.

Portrait of Francisco de Saavedra, Francisco de Goya, 1798

Recent treatment of the full-length *Portrait of Francisco de Saavedra* by Goya (Courtauld Gallery, London) included removal of a browned, aged coating and revealed that the whole surface was covered with multiple shallow protrusions, each topped with a spot of dark brown material. While dense populations of protrusions were visible in brown painted areas, the visual effect of the brown spots was more pronounced in passages of light-colored paint. Figure 14.5a shows the low protrusions in an area of paint in the foreground, with one group shown at high

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[4] Indicated in a cross section by positive Amido Black stain for protein.

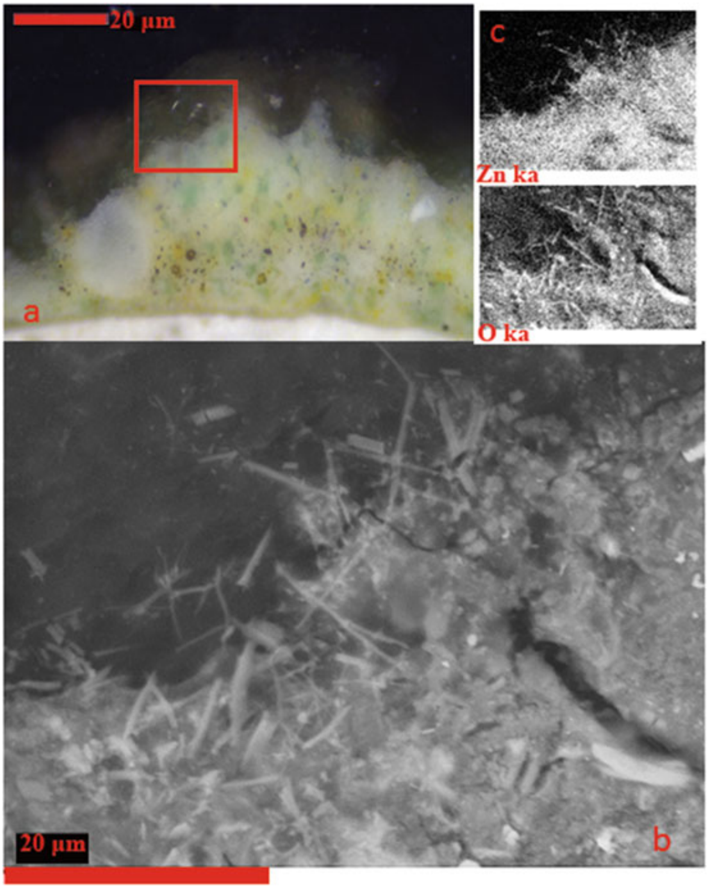

Fig. 14.4 (**a**) Cross section from zinc soap-containing paint and browned coating from *Wolmer Wood*. (**b**) SEM-BE image of the interface between the paint and the coating from the area of the cross section indicated in (**a**) by a red box. (**c**) Elemental mapping of the same area showing crystals containing elemental Zn and O at the paint-coating interface

magnification in 5b. A SEM secondary electron (SE) image of the surface of one protrusion is shown in 5c highlighting the globular shape of these protrusions, with convex or concave profiles. In cross section (Fig. 14.5d), the subsurface features of the protrusion become evident, with areas that are medium rich and devoid of pigment particles and areas of recrystallization of high atomic number species.

Analysis of paint cross sections from representative areas using light microscopy and SEM-EDX indicated iron oxide earth pigments, aluminosilicates, calcium sulfate, chalk, and lead carbonate in the ground. The cross sections included characteristic lead soap aggregates in various stages of recrystallization as reported in other studies of oil paintings. Similar protrusions with brown spotting have been observed on the surface of other portraits by Goya painted in the last decade of

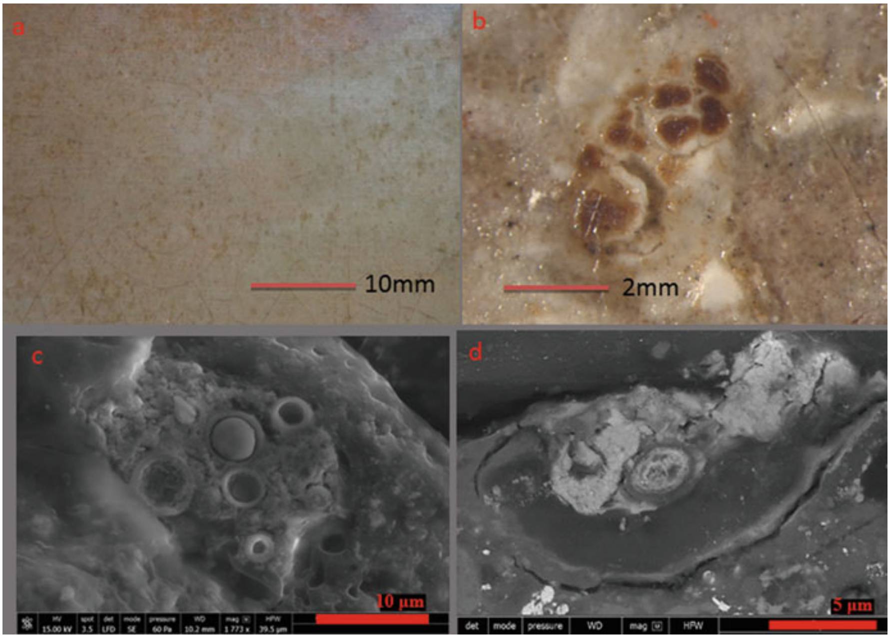

Fig. 14.5 (**a**) Detail of the foreground paint surface from *Portrait of Francisco Saavedra* showing spotting. (**b**) Detail from (**a**) showing a group of protrusions topped by brown spots. (**c**) SEM secondary electron image of the surface of a similar protrusion to that seen in. (**b**), (**d**) SEM-backscattered electron image of a cross section from a protrusion showing the subsurface features of the protrusion in (**c**)

the eighteenth and early in the nineteenth century[5] (Puig et al. 2016). The presence of identical surface degradation on works by Goya with different provenance and material histories points to factors related to the composition of the paint, ground or possibly the first coating applied after the work was completed.[6] There are records of the use of oil and resin varnishes in Spain from the early seventeenth century. In the case of Goya, apart from a comment he made in 1800 on the treatment of one of his paintings that allegedly included the use of egg white varnish (Veliz Bomford and Aterido 2016), there are no extant documents that refer to his vanishing practice.

When combined with empirical evidence from the conservation history of the works, condition of the surface and material analysis of both *Wolmer Wood* and the *Saavedra* portrait, the possibility arises that the application of an oil or oil-

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[5] Enrique Quintana, Head of painting conservation, Museo Nacional del Prado, personal Communication 2015, and firsthand observation of contemporary portraits by Goya in the conservation studio of the Museo Nacional del Prado. Lead soap aggregates in paint samples from selected paintings by Goya in the Prado were confirmed by analysis carried out by Maria Dolores Gayo, head of the Museum's Scientific Department.

[6] Enrique Quintana, personal communication 2015.

resin varnish may contribute to the formation of metal soaps at the surface of the paintings. This hypothesis is plausible considering that oil-containing coatings – whenever they are applied in the lifetime of a painting – provide a source of free fatty acids that may react with metal ions at the paint surface. While the resin component of the coatings on these paintings may be removable using the range of solvents typically used for varnish removal, the oil component has the potential to form insoluble metal carboxylates. It is also plausible that acidic components in aged natural resin coatings may react with alkaline pigments in the underlying paint, or in a tinted varnish, with pigments that contain reactive ions to form soaps. This hypothesis requires further investigation.

Female Nude, Amedeo Modigliani, c.1917

Another physical manifestation of soaps on the surface of oil paintings is exemplified by *Female Nude*, by Modigliani (Courtauld Gallery, London) (Fig. 14.6). Under magnification the surface shows pinpoint losses exposing the white priming in dark-colored areas (Fig. 14.6b), while raking light observation highlights several scattered protrusions in the flesh tones (Fig. 14.6c). A cross section (6d) shows a layer of glue size, indicated by the arrow, followed by a layer of lead white and chalk (with blue pigments) superimposed by a blue-grey second ground layer containing barium sulfate, zinc oxide (or sulfide), and carbon black. The flesh paint contains lead white mixed with vermilion and shows a surface with aggregates of zinc soaps and lead soaps (typically 20–100 µm diameter) formed on the peaks of impasted

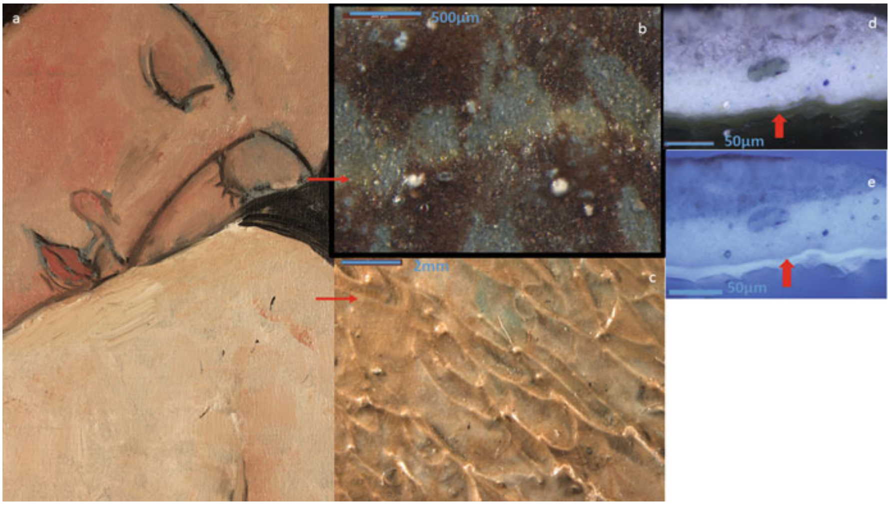

Fig. 14.6 (**a**) Detail of flesh paint from *Female Nude.* (**b**) Detail of the blue-grey ground with metal soap aggregates indicated by arrow. (**c**) Detail of flesh paint with lead soaps indicated by arrow. (**d**) A cross section from the double ground with a layer of glue size indicated by the arrow. (e) The same cross section in UV light

paint (indicated by a red arrow in 6c). Areas of exposed ground contained both lead and zinc soap aggregates.

The even distribution of zinc and lead soap aggregates in both varnished and unvarnished areas (the latter in a strip that had remained unvarnished and protected by the frame rebate) suggests that in this case the formation of lead and zinc soaps was not influenced by the surface coating.

14.3 Paint Delamination

Two works, painted on different supports, highlight conservation challenges posed by delamination of paint layers that can be caused by zinc soaps.

The Pilgrims Rest Hotel, Robert Brooks, d.1995, private collection, oil on cotton duck canvas

The painting primed with titanium white in oil has a history of blind cleavage and severe delamination between paint layers. It was first examined and treated at the Courtauld in 2009 and then treated again in 2013 and 2016.[7] The loss of cohesion between paint layers is caused by soaps formed from paint containing zinc oxide, confirmed by FTIR analysis. In the most pronounced areas of delamination, intralamellar fracture between layers containing zinc oxide was evident, rather than between the paint and the ground that did not contain zinc. Similar delamination phenomena in painted art have been observed by other authors including Van der Weerd et al. (2003); Rogala et al. (2010); Osmond G (2019); and Raven et al. (2018).

Man Clearing Snow Red Square, Ralph Lillford, 1986 private collection, acrylic and oil on hardboard

Similar delamination was observed in a painting by Ralph Lillford which was first examined and treated in 2009 and again in 2017. The composition was painted over another underlying scheme, on the smooth side of a hardboard support primed with titanium white, chalk, and kaolin. Like the painting by Brooks, delamination had occurred between and within paint layers containing zinc and/or calcium soaps (Fig. 14.7).

Cross sections indicated that the source of fatty acids for zinc soap aggregates visible in the upper paint layers could be a medium-rich underlayer of carbon black paint, or alternatively they may be formed from polar degradation products of hydrolysis of the oil medium at the paint surface. Metal soaps formed by reaction between zinc oxide and stearic acid, a chemical process that generates water, may also have favored ongoing soap formation in the paint film (Osmond 2014). The formation of a layer of zinc soaps that led to delamination, considered in the light of similar observations in published case studies, raises the question of what conditions

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[7] Report CIA: 1998 2009, and notes on condition and re-treatment in 2009 and 2013, Department of Conservation & Technology, Courtauld Institute of Art.

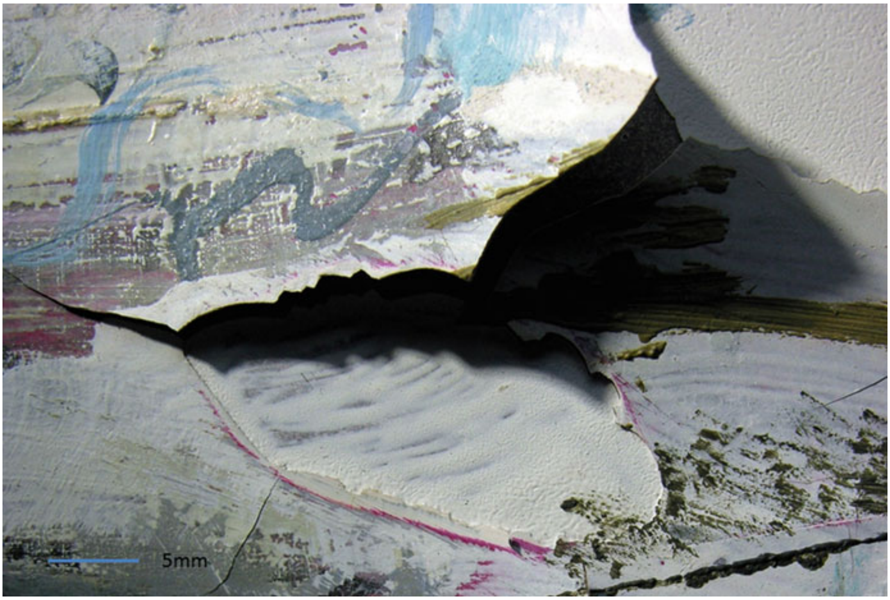

Fig. 14.7 Detail of flaking paint from *Man Clearing Snow Red Square*, showing delamination in areas of zinc oxide-containing paint

favor the formation of zinc aggregates or formations that result in delamination. The technical challenges for characterizing the coordination of fatty acids in zinc soaps within paint layers in works of art include identification of different kinds of oil media based on fatty acid profiles. This question is informed by investigation of model paint systems (Osmond 2014; Hermans et al. 2015).

14.4 Metal Soaps and Water Sensitivity in Unvarnished Modern Paints

Building site, Oxford Street, Frank Auerbach, 1959–1960, Tate Gallery, London [catalogue number T00418], oil on unprimed hardboard

Recent analytical studies of modern oil paintings that present water sensitivity on surface cleaning[8] raise questions about the role of metal soaps in relation to the response of paint to polar solvents. *Building site, Oxford Street* is thickly painted in oil on an unprimed hardboard support. The unvarnished surface includes passages of glossy and matte paint, reflecting different proportions of oil to pigment.

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[8] Bay L (2015) Documenting water-sensitive oil paintings in the Tate Gallery. Final Year Project Department of Conservation & Technology, Courtauld Institute of Art, London.

Tests showed that pigment was removed from glossy paint after three to five rolls of a cotton swab with deionized water. Samples from the painting prepared as cross sections showed a skin of organic material at the surface together with fatty acid efflorescence. FTIR spectra from surface material exhibited split carbonyl absorptions at 1737 and 1713 cm^{-1} indicative of glycerides and free fatty acids in partially hydrolyzed oil and indicated the presence of polar azelaic acid.[9] Subsurface paint contained zinc stearate (indicated by absorption at 1539 cm^{-1}) and also iron oxide pigments extended with coarsely ground kaolin, gypsum, chalk, and barium sulfate. This combination of materials absorbs a significant quantity of oil medium and contains relatively few reactive metal ions, thus providing a source of fatty acids. However, the possibility that metal stearates including palmitates and free fatty acids were added to the paint by the manufacturer may also contribute to the availability of an excess of unreacted free fatty acids that could account for the observed surface phenomena (Burnstock and van den Berg 2014). The influence on water sensitivity of metal soaps added by the manufacturer and those formed in situ from inorganic pigments and fatty acids from the oil medium is the subject of current investigation.

14.5 Considerations for Treatment

The different forms of soaps and their relationships to the paint surface are an important consideration in formulating treatment approaches, examples of which are discussed below in relation to the case studies described in the preceding sections.

14.5.1 The Use of Aqueous or Hygroscopic Materials for Consolidation, Cleaning, and Lining

Where flaking or delamination is caused by zinc soaps, it is possible that the introduction of aqueous adhesives for consolidation may promote hydrolysis of oil media and further soap formation. This clearly conflicts with the objective to readhere delamination within a zinc soap-containing paint layer. A consideration of the treatment histories of the paintings by Brooks and Lillford (described in Sect. 14.3) supports this hypothesis.

The first treatment of the Brooks carried out in 2009 included consolidation of areas of flaking paint using a 20% solution of Aquazol 500 in deionized water applied with a small brush. The delaminating areas were gently massaged using a heated spatula at 45 °C and weighted overnight. The necessity for repeated treatment suggests that the paint was actively delaminating. Based on recent research that suggests that zinc oxide will readily form soaps in oil media and in an aqueous environment, it is possible that in this case the use of an aqueous adhesive or

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[9] Analysis of the surface and bulk paints was carried out by PhD candidate Judith Lee using SEM-EDX and FTIR mapping and electrospray ionization mass spectrometry (ESI-MS).

hygroscopic resin for consolidation might have exacerbated the delamination by enhancing the formation of soaps (Arslanoglu 2004). In the case of the Lillford painting, areas of flaking retreated using BEVA 371 has proved effective.

Further investigation of the use of nonaqueous consolidants for this purpose may provide useful guidelines for conservation treatments. In practice, there may be a range of factors that influence the choice of adhesives for consolidation of flaking paint. They include the sensitivity of the paint to the carrier solvent, access to the cleavage that may require highly dilute solutions or pre-wetting with solvent, and risk of optical changes during removal of residual adhesive from unvarnished paint surfaces.

The influence of moisture on soap formation in paintings, including acute short-term contact with moisture as part of conservation treatment, has not been systematically investigated. In addition to consolidation using aqueous media, relevant procedures would include lining and the use of water-based cleaning methods. Also likely to be influential are aspects of artists' techniques and materials, such as canvas preparation (by artist or manufacturer) using a hygroscopic size layer, as was the case in Modigliani's *Female Nude* (Sect. 14.2.2). Other factors influencing soap formation include exposure to humid environmental conditions and absorption of moisture by the size layer or possibly the application of an aqueous protein interlayer (as was the case in *Wolmer Wood*, Sect. 14.2.2). All of these factors may provide a favorable environment for hydrolysis of the overlying oil paint (Osmond et al. 2014). *Female Nude*, painted in c1917, was lined (for the first time) with a wax-resin adhesive in the late 1950s; in the absence of experimental study, it is reasonable to speculate that this treatment has reduced the response of the size layer to increased humidity and thus reduced the risk of further hydrolysis of paint that may lead to soap formation. However, in this work the texture of the flesh paint and significant areas of exposed ground are pronounced due to the formation of soaps, whether intended or not, and this will be an important consideration in the plan for future treatment.

In cases where soap formation is the result of direct contact with moisture evidenced by water staining or its consequences (such as mold formation, in the case of the Ethel Walker described later in Sect. 14.5.3), it is clear that preventive conservation measures, such as dusting to remove fungal spores, the incorporation of backboards and glazing, or control of environmental moisture exposure by air-conditioning, reduces the risk of further deterioration.

14.5.2 Surface Cleaning of Unvarnished Water-Sensitive Paintings

Building site, Oxford Street (discussed in Sect. 14.4), in common with other twentieth-century unvarnished oil paintings, incorporates passages of paint that exhibit sensitivity to water. This precludes the use of water to remove dirt from their surfaces and limits conservators to dry cleaning. Alternative methods for cleaning using apolar solvents are ineffective in removing the polar fractions of soiling or dirt imbibed in the skin of medium at the paint surface.

Recent studies have examined the efficacy of rigid gels such as agarose for topical delivery of cleaning reagents. Such methods, together with the use of synthetic absorbent microfilament materials such as Evolon,[10] offer a method of cleaning with significantly reduced mechanical action compared with conventional cotton wool swabbing. Another approach is the use of microemulsions tailored for cleaning water-sensitive paints. Chung et al. (2017) examined a range of microemulsions for removal of artificial dirt from samples of moderately aged water-sensitive Winsor & Newton paints and found some formulations were moderately effective. However the clearance of non volatile components of these materials and the short or longer term effects of residues on the painting have not been systematically investigated.

New options for surface cleaning water-sensitive paints may be to introduce reactive ions to trigger the reaction between free fatty acids to form insoluble salts that might then be resistant to water swabbing. However, the ethics and practicalities of this approach considering the possibility of irreversible optical changes to the paint surface require careful consideration and further research.

14.5.3 Removal/Treatment of Metal Soap Efflorescence and Crusts

The removal or reduction of insoluble metal soap crusts can be achieved using aqueous solutions of chelating agents, formulated with specific concentration and pH, and applied using a range of methods. Sawicka[11] addressed the methods for removal of different forms of superficial white surface efflorescence in paintings using ethylenediaminetetraacetic acid (EDTA). She also formulated guidelines in diagram format for a sequence of treatment options that might be useful for conservators faced with treating paintings with metal soap hazes or crusts (Fig. 14.8). Likewise Van Loon et al. (2019) developed a procedure for determining the feasibility of removing these inorganic or semi-inorganic degradation layers. A first step would be SEM-EDX analysis of a cross section to determine the nature of the interface between the crust and the paint surface. The extent to which the coating or crust has become part of the paint surface will limit what can safely be removed. Another approach may be to try to saturate the surface using low molecular weight resins and/or to locally retouch the disfiguring areas of the painting. If the areas affected

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[10] http://www.preservationequipment.com/Catalogue/Conservation-Materials/Materials-and-Fabrics/Evolon-Microfilament-Material

[11] SawickaA (2014) Clearing the "Haze" of Inorganic Efflorescence An investigation into the formation of lead soap efflorescence and the viability of its removal by means of the chelating agent Ethylenediaminetetraacetic Acid, Final year project, Department of Conservation &Technology, Courtauld Institute of Art, London.

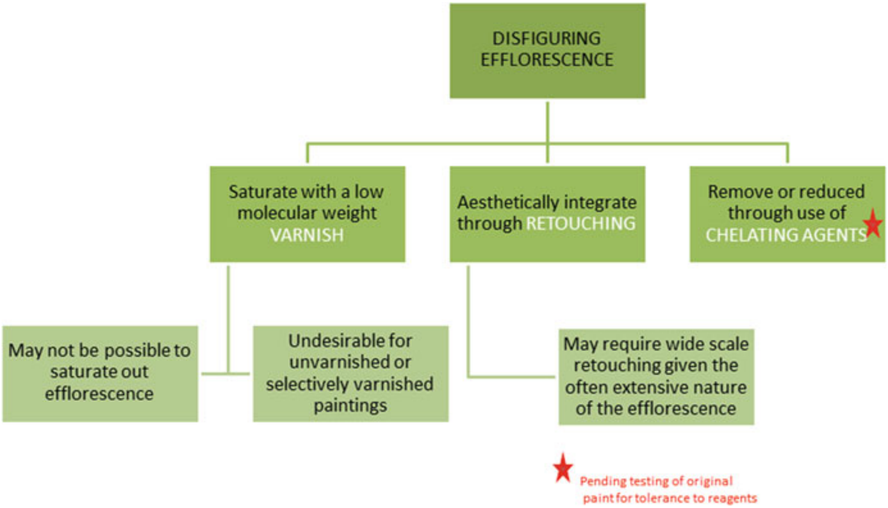

Fig. 14.8 Diagram of guidelines for a sequence of options for treating paintings with metal soap efflorescence and soap hazes (Adapted from Sawicka et al. 2014)

by efflorescence are too large, or too disturbing, the option to remove or reduce the crust can be achieved using an appropriate chelating agent. The choice of chelant depends on the preference for chelation of specific metal ions and lower chelation power for other metal ions present in the original paint. Their application should utilize solutions of pH range that optimize the chelation of specific metal ions in the soaps and present low risk of hydrolysis of the oil medium. Table 14.1 provides a list of stability constants which offers a guide for the choice of chelant, based on relative preferences for formation of stable metal-chelate complexes. Although the table presents a wider range of options, studies of the application of chelating agents for paintings have focused on the use of citrates for surface cleaning (Morrison et al. 2007) and EDTA for removal of soaps hazes (Sawicka et al. 2014). Both have shown that the pH, concentration of chelant, and method of application are critical in tailoring the reagent for purpose. Possible drawbacks include inefficient clearance of chelating agents, in particular where they are gelled (usually with a cellulosic thickener); the risk of affecting the equilibrium of the paint film by acute moisture exposure; and if the solution is not precisely tailored or applied, chelation of metal ions in the paint.

It was possible to reduce a brown layer containing zinc soaps from the surface of *Wolmer Wood* using EDTA solutions. Images of the surface taken during treatment illustrate the significant challenges involved in a kind of cleaning that necessitates the removal, or partial removal, of a coating that has become imbibed in the painting. There are pits left where soaps are removed, together with the residues of the coating that were not readily removable (Fig. 14.3b). EDTA solutions were also effective in removing lead soap efflorescence from the drapery of *Carolina Ewen* (Sect. 14.2.1).

Table 14.1 Stability/equilibrium constants for selected metal-chelant complexes (log K). The higher the log K value the more tightly the metal ion will be bound to the chelating agent, and the more likely that the complex will be formed (Martell and Smith 2003)

Metal ion	EDTA	GLDA	DTPA	HEDTA	STPP	Citric Acid	EDG
Al^{3+}	16.4	12.2	18.6	14.4		7.0	7.7
Ba^{2+}	7.9	3.5	8.7	6.2	3.0	2.8	3.4
Ca^{2+}	10.7	5.9	10.8	8.1	5.3	3.2	4.7
Cd^{2+}	16.5	9.1	19.0	13.7	6.5	4.2	7.4
Co^{2+}	16.5	10.0	18.8	14.5	6.9	4.4	8.0
Cu^{3+}	18.8	13.1	21.2	17.4	8.7	14.2	11.8
Fe^{2+}	14.3	8.7	16.2	12.2	2.5	3.0	6.8
Fe^{3+}	25.1	11.7	28.0	19.7		11.9	11.6
Hg^{2+}	21.5	14.3	26.4	20.1			5.5
Mg^{2+}	8.8	5.2	9.3	7.0	5.7	3.2	3.4
Mn^{2+}	13.9	7.6	15.2	11.1	7.2	3.5	5.5
Ni^{2+}	18.4	10.9	20.1	17.1	6.7	4.4	9.3
Pb^{2+}	18.0	10.5	18.8	15.6		6.5	9.4
Sr^{2+}	8.7	4.1	9.8	6.8	4.4	2.9	3.8
Zn^{2+}	16.5	10.0	18.2	14.6	7.6	4.5	8.4

As determined at an ionic strength of 0.1 M at 25C. *EDTA* ethylenediaminetetraacetic acid, *L-GLDA* glutamic acid N,N-diacetic acid, *DTPA* diethylentriaminetetraacetic acid, *HEDTA* hydroxyethylethylenediaminetriacetic acid, *STTP* sodium tripolyphosphate, *EDG* ethanoldiglycinic acid

However, in this case each area where an aggregate of lead salt crystals had been removed left a dark spot that required retouching. Using a combination of EDTA in cellulose-thickened gels, it was possible to reduce the lead soap crusts in the foreground of *Return from the Front* (Sect. 14.2.1) to some extent, but application of the reagent close to the paint surface proved too risky. In all these cases, as in all cleaning campaigns, the skill and judgment of the conservator carrying out the treatment resulted in an interpretation of the condition of the composition and texture of the surface with the ultimate aim to make the composition more legible. The success of treatments depended on the extent to which the coating or crust has become part of the painting surface, limiting what can safely be removed. When re-saturated with a new varnish, the composition of *Wolmer Wood* and the drapery of *Carolina Ewen* and the foreground of *Return from the Front* became more readable, although the compromises included exposing surface deterioration that necessitated aesthetic reintegration.

The influence of environmental moisture and the use of hygroscopic materials in paintings on the formation of lead soaps are highlighted in several of the case studies discussed in this chapter and more comprehensively in a recent review by Cotte et al. (2017). This link is important in relation to the approaches to both active and preventive conservation treatments, discussed below. Examples include soaps that formed in paintings exposed to humid environmental conditions, heat, and light (Keune et al. 2016). The moisture absorption properties of zinc oxide pigment may influence the tendency for soap formation in oil media by enhancing hydrolysis (Osmond 2012). This may have played a role in the formation of zinc and also lead soaps in *Female Nude*, which was painted on an open weave canvas prepared with a substantial layer of hygroscopic glue size. It is possible that this size layer may have provided a reservoir of moisture in damp conditions which, together with the hygroscopic character of zinc oxide, created the ideal conditions for formation of soaps. A similar stratigraphy has also been observed in a painting discussed by Osmond et al. (2014).

The Pilgrims Rest Hotel (Sect. 14.3) suffered cleavage between paint layers due to metal soap formation. The expansion and contraction of the canvas in response to changes in environmental moisture and to tapping out the stretcher keys had caused cracking in brittle zinc oxide-containing paints. The brittleness of zinc-containing paints poses a problem in particular where cupped and flaking paint is combined with shrinkage and deformation of the support.

Evidence for the effect of moisture on metal soap formation is exemplified by the Courtauld Gallery's *Draped Woman standing by a Mantlepiece* painted in 1938 by Ethel Walker (Burnstock et al. 2016).[12] The painting in oil on commercially primed canvas is unvarnished and displayed on the reverse of a stretcher with the unprimed side painted with another image facing outward. The painting has been stored and displayed with a backing board since its acquisition in 1973. That the painting had been exposed to moisture during the course of its history was evident when technical examination showed the presence of developed fungal hyphae. The identification of particularly concentrated areas of lead soaps in areas where fungal hyphae are present pointed to the favorable effect such conditions have on the development of both mold and lead soaps.

14.5.4 Treatment of Surface Aggregates

Numerous dark topped lead soap protrusions at the surface of the *Saavedra* portrait (Sect. 14.2.2) were particularly disturbing in the areas of the light-colored background paint, the flesh, and the blue and other pale-colored draperies. Tests showed that the brown spots were insoluble in the range of solvents used to remove varnish, but they could be reduced by repeated application of an oil-swelling solvent (such as n-methyl-2-pyrrolidone, NMP) in gelled form or removed together with some of the underlying lead soap mass using 2% EDTA in deionized water. The use of this solution applied in a gel was effective in removing the spot, by undercutting and removal of the surface of the underlying protrusion. The difficulties of limiting the application of the gel precisely to the spot and the clearance of the gel were challenging in this case. After consultation with conservators at the Prado, it was

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decided not to remove the material but to disguise the most disturbing dark spots with retouching.

The technical study of *Female Nude* was carried out in advance of future treatment. The characterization of soaps in the paint and ground and their significance in relation to the original paint texture, together with an understanding of the role of the varnish that is likely to have been applied at the same time as the wax-resin lining, will influence the approach to cleaning and interpretation of the work.

In all the cases discussed, removal or retention of metal soaps during cleaning required an interpretation of the paint surface that involved removal of surface material. Treatment decisions involve finding a balance between the risks to the paint film and the aesthetic gains. The interpretation of an image obscured by soap crusts or optically disturbing surface protrusions presents practical, aesthetic, and ethical challenges for conservators. Dark spots, similar to those found on the *Saavedra* portrait, are present on the surface of many paintings of different dates, including works in egg tempera and other media. These spots often remain on the paint as insoluble residues left during varnish removal using polar solvents and can sometimes be removed or reduced using an oil-swelling solvent, used together with a polar solvent or alkaline reagent in solution or gelled form. The question, however, of whether or not removal should be attempted is interesting to consider in the context of the acceptance, within contemporary conservation ethics, of other visual alterations such as fading of paint containing organic lakes, discoloration of smalt, and increased transparency of paint. More pertinent still is the decision generally taken not to remove areas of superficial degradation, such as the blackening of vermilion or browned copper-green paints, in order to reveal the better preserved material beneath.

14.6 Conclusion

The aim of this chapter has been to highlight various manifestations of metal soaps in paintings, add to the already significant body of published information and help to inform conservators' assessment of the condition of a work, and guide approaches to conservation. The strategies for treatment of the paintings introduced here present a range of options (and compromises) that require careful evaluation.

A combination of empirical and analytical evidence is presented that supports the notion that metal soaps form where fatty acids and metal ions are available; the idea that the introduction of new sources of fatty acids and/or metal ions may favor the mobility or reorganization of metal soaps within the painting structure; the suggestion that raised humidity and direct contact with water favor the formation of metal soaps; and the theory that the different physical manifestations of soaps are dependent upon chemical environment, the distribution of reactive species within the paint film, together with external environmental factors. Many of these ideas have been investigated in detail in previously published studies and in other contributions in this volume.

A number of questions arise from these studies that may influence approaches to treatment and would be informed by further research. The question of the time it takes for metal soaps to form in oil paint is pertinent to the question of whether or not artists anticipated changes in surface texture and in helping to date later interventions. Increased understanding of metal soap formation has a bearing therefore on interpreting artists' intentions and on the formulation of treatment rationales that consider the ongoing formation of soaps in paintings.

There may be some commonalities that can be identified regarding the predisposition of oil paints to specific kinds of soap formation, such as zinc soap aggregates, or lamellar formations that might lead to delamination or cleavage between paint layers. The role of metal soaps, formed in or added to modern oil paints, and their relationship to water sensitivity in unvarnished paintings is another area of current research.

Recognition of surface changes and their causal agents is essential for designing effective and appropriate conservation treatments. The removal of metal soap crusts and formations presents new ethical considerations for conservators because they constitute degradation products that have formed from original painting materials. However, there is currently limited research on effective methods for removal of residues of nonvolatile components of cleaning reagents including chelating agents, surfactants, and other materials applied in solution, poultice, or gel form. The long-term consequences of residual materials on works of art are a critical concern.

Good conservation practice requires chemical knowledge of the causes of deterioration, the design of an appropriate treatment, and the means to carry it out. The arsenal of methods and materials for cleaning paintings has been greatly enhanced in the last 30 years by practitioners such as Richard Wolbers (Angelova et al. 2017), and there is an awareness of the need to consider appropriate treatment for paintings with different physical histories and current contexts. Paramount is the judgment and skill of the conservator, who evaluates the evidence, takes the decisions, and undertakes the treatment of the work.

Acknowledgments Klaas Jan van den Berg (RCE/University of Amsterdam), Bronwyn Ormsby and Judith Lee (Tate, London), Jae Youn Chung (Hamilton Kerr Institute, Cambridge), Lucia Bay (Philadelphia Museum of Art), Alex Ball and Tomasz Goral (Natural History Museum London), William Luckhust (Kings College London).

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