An Investigation into the Viability of Removal of Lead Soap Efflorescence from Contemporary Oil Paintings

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Abstract Metal soap efflorescent hazes and crusts are one of the most visually disturbing of all metal soap related alterations in paintings. The phenomenon presents particular challenges for conservators as the surface deposits that form are insoluble and intimately bound with the paint film. The superficial deposits accumulate following migration of metal carboxylates, a product formed within the paint film from reaction of free fatty acids with metal ions from pigments and/or driers. Upon deposition at the surface, the metal carboxylates undergo a process of remineralisation, the products of which are determined by the atmospheric conditions that the painting is exposed to. The material can appear optically similar to the whitish haze of organic efflorescence though manifestations also range from

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crystalline clusters to thick crusts, and in some cases the painting may consequently be rendered partially unreadable. This study aimed to investigate the removal of visually disturbing lead soap efflorescence with Ethylenediaminetetraacetic acid (EDTA), which sequesters the lead ions from the remineralised crust. Through a careful balance of variables such as pH, concentration and application, it is feasible to thin the superficial material significantly. By this means it is possible to saturate the surface of the paint film and render the previously disfiguring efflorescence transparent. Paintings previously treated with this method show no signs of recurrence and thus it appears to be a viable, long-term treatment option.

Keywords Efflorescence • Lead soaps • Free fatty acids • Remineralisation • Treatment • Ethylenediaminetetraacetic acid

Introduction

The Problem of Lead Soap Efflorescence

From the moment of execution, paintings undergo numerous chemical and physical processes, through which the paint film cures, ages and subsequently degrades. The nature of the surface of the painted picture is thus determined to a large extent by the chemical and physical processes that take place within the paint film. These processes within the three-dimensional network of a mature paint film can affect the structure's stability and may result in the migration of mobile components within the paint layers or to the surface of the painting.

This migration is the source for three distinct surface phenomena: metal soap aggregation, fatty acid efflorescence and metal soap efflorescence. Whilst the former have been the subject of extensive research,[1] and are thus commonly identified, metal soap efflorescence, namely lead soap efflorescence, has only recently been investigated (Van Loon et al. 2011; Van Loon 2008; Keune et al. 2007). Limited recognition of lead soap efflorescence as a distinctly different degradation phenomenon is due to the small number of analytical studies undertaken. The matter is further complicated by the visual similarity of the effects of some lead soap efflorescence to that caused by surface accretions of free fatty acids. The difference in solubility of the degradation products on empirical testing has provided criteria for identification of different causes of light scattering at the surface of paintings.

The phenomena of unknown cause can be described in general terms: *whitening*, *hazing*, or *white surface depositions*. However, clarification of specific terms may lead to greater enlightenment regarding the mechanism and appearance of lead soap

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[1] Research carried out as part of the NWO priority programme MOLART (Molecular Aspects of Ageing in Painted Works of Art) (1995–2001) and the De Mayerne programme (2002–2006) at the FOM Institute, AMOLF.

efflorescence. The following terms clarified by Van Loon (2008), are considered appropriate, although meanings may differ from previous applications:

Chalking implies light-scattering of the surface film due to the breakdown of binding medium.

Blooming describes the migration of extractable components within the paint film and subsequent surface deposition, typically applicable to white organic precipitates.[2]

Efflorescence also refers to the process of migration and deposition, though is more specific for inorganic deposits.

In this paper, the phenomenon will thus be refered to as efflorescence, and quantified as inorganic/metal soap or organic/fatty acid to avoid confusion.

Hypotheses for the Formation of Lead Soap Efflorescence

The formation of metal carboxylates is a normal reaction product of mobile fatty acids with metal ions from pigments and/or driers. Lead and zinc carboxylates are most commonly identified, likely due to the fact that lead- and zinc-containing pigments are known to promote the de-esterification of the paint, although other forms may be encountered according to the pigments present.[3] When uniformly dispersed, the metal soaps are thought to confer flexibility to the paint film, though there appears a tendency towards aggregation, resulting in the large occluded masses of metal soaps which expand and finally break through the surface. Lead soaps may also migrate without aggregation and migrate towards paint-air interfaces, such as the surface of the paint film or cracking within a paint film. Upon deposition at the surface, the lead soaps also undergo a process of remineralisation, precipitating and crystallising in an energetically favourable orientation due to further reaction with atmospheric gases. The degree and nature of the remineralised salts are dependent on a variety of factors including the nature of the soap, the paint composition, treatment history and the environment to which the painting has been exposed (Van Loon 2008). It has been postulated that tendency towards migration without aggregation may be related to a low degree of metal coordination within the paint layer and susceptibility for acid hydrolysis (Noble and Boon 2007). This may account for the observation of lead soap efflorescence primarily on highly

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[2] Though blooming is defined in this manner by both Van Loon (2008) and Akerlund (2012), the term has also been widely applied to visual changes in the varnish layer, most often due to penetration of moisture.

[3] For example potassium soaps have been demonstrated as a result of the leaching of potassium from smalt (Spring et al. 2005).

oil-absorbent porous paint layers containing pigments such as chalk, lakes, carbon black and earth pigments identified by Van Loon (2008).[4]

Efflorescence in Nineteenth- and Twentieth-Century Paintings

The propensity of paintings from the nineteenth and early twentieth centuries to metal soap efflorescence is likely to relate to the specificities of the materials employed. Following the invention of the collapsible paint tube and the opening of the first factory for pigment preparation, a number of pivotal developments were made in commercial paint production, including the incorporation of additives and manufacturing methods that affected the oxidation process, promoted hydrolysis and introduced or increased the proportion of fatty acid containing materials.

Developments in the composition of commercially prepared ground layers may be an important causal factor: the incidences of lead soap protrusions, efflorescence and associated variable translucency observed on unpainted, pre-primed canvases in the Olana archive are hypothesised to have been caused by migration of lead ions from ground or priming layers (Zucker 2007). The demand for a uniform, smooth surface that would absorb excess oil, supple enough to be rolled for storage and shipping, led to modification of recipes often at the expensive of quality. Given the profit motive that dominated the concerns of artists' colourmen, this modification included the addition of extenders, and unstable materials, which may have influenced the formation of degradation products. For example, the technical and economic difficulties in mass producing oil priming, which requires time to dry and mature, led to the use of power siccatives, and the brittleness which these imparted to the paint film was in turn counteracted through the addition of saponified fats and waxes.

Contemporary treatise, including Field's *Chromatography* (1862) and Church's *The Chemistry of Paints and Painting* (1890), discuss the use of sugar of lead (lead acetate drier), both incorporated in paints and strewn on pictures whilst wet, to promote quick drying. Notably, their warning of resulting 'efflorescence' is remarkably accurate; Church describes one of the results of the addition of lead acetate as:

> . . . the production of an immense number of small spots in the picture, sometimes appearing through the surface-varnish in the form of a white efflorescence. This efflorescence consists at first of lead acetate in crystals, but these soon attract carbonic acid from the air and become lead carbonate, which, in its turn, is changed into lead sulphide by the action of sulpheretted hydrogen.

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[4] Ongoing research is being undertaken as part of the NWO Science4Arts PAinT project by Van Loon and Keune (http://www.s4a-paint.uva.nl/research-topics). Research will focus on the timescale of the phenomena and the identification of other key factors for soap formation migration, dissolution, recrystalisation and efflorescence in oil paint.

Paint formulations of the period are also critical to the formation of efflorescence as they offer a greater source of free fatty acids (Akerlund 2012). The inclusion of chemically inert bulking additives including barium sulphate, hydrated aluminium silicate and calcium carbonate, and the substitution of titanium dioxide for the carboxylate-forming zinc- and lead white, passively promote efflorescence through their exclusion from ionic reactions within the paint film.[5] Furthermore the absorbency of chalk in particular necessitates an oil-rich paint film, and the pigment-volume concentration of certain paint films illustrate that they effectively provide reservoirs of free fatty acids due to lack of metal coordination (Hinde et al. 2011; Ferreira et al. 2011). Alternatively components of efflorescence may themselves be included as additives, Tempest et al. (2013) observing a proportional relationship between the presence of stearic acid additives and of fatty acid bloom, and Mills et al. (2008) noting the presence of metal stearate additives as conducive to efflorescence and metal soap aggregation.

Treatment of Lead Soap Efflorescence

Suitable treatments for lead soap efflorescence have not been thoroughly investigated. The disfiguring material is insoluble in the range of organic solvents utilised for the removal of varnish, old restorations and indeed fatty acid efflorescence, and its intimate integration with the underlying paint precludes safe mechanical removal. The conservator thus faces the challenge of developing alternative methods. Effective removal of inorganic efflorescence from paint surfaces has not been considered feasible thus far, without compromising original paint beneath.

The most common approach is to reduce the degree of whitening by saturation with a low-viscosity resin, which fills the voids and micro-fissures of the surface film, reduces light-scattering and thus renders the efflorescence more transparent. Saturation however is not always feasible; it may be undesirable, as in unvarnished or locally-varnished paintings, or indeed impossible. In the latter scenario, surface whitening may be aesthetically integrated through retouching, though this could lead to large-scale covering of original paint, given the commonly widespread nature of the efflorescence. Van Loon (2008) concludes that in this case the only option is reconstruction by retouching. However, previous conservation treatments highlight an alternative. Chelating agents including triammonium citrate, diammonium hydrogen citrate and ethylenediaminetertraacetic acid have been deemed successful in a number of treatments aiming to remove inorganic salts from the surface of paintings (Morrison et al. 2007; Slavin 1990; Treatment reports CIA 1842 and CIA

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[5] Hinde identified the inability of titanium dioxide to form stabilizing carboxylates as a key factor in the formation of fatty acid efflorescence in *Composition* by Serge Poliakoff (1956) (Hinde et al. 2011).

1939) though the action and the nature of the resultant surface remains unclear. This study investigates the application of the selected chelant for the removal of lead soap efflorescence in relation to these unresolved issues.

Introduced for the surface cleaning of paintings in the 1980s, chelating agents are now widely employed tools at the conservator's disposal, though concern has been raised over the use of chelants on painted surfaces. Pigmented films typically contain cations capable of sequestration, and thus it is critical to select an appropriate chelating agent based on an intimate knowledge of the material constituents of both the substance to be removed and the substrate it is to be removed from. For the removal of lead-containing material, the criteria proposed would thus be a chelant with a strong affinity for lead ions, a weak affinity for other metal ions potentially present in the underlying paint film and the ability to chelate in a pH range recommended for use on oil paint films, generally reported as a pH range from 5.5 to 8.5.

Based on these parameters the chelating agent ethylenediaminetetraacetic acid (EDTA) was selected for trial. Thorough knowledge of its chelation mechanism and parameters of use are published in the literature of the detergency, medical and soil industries (Hong and Jiang 2005; Kim et al. 2003; García et al. 2011). The chelant has a strong affinity for lead ions to enable efficient chelation of the efflorescent material within the pH range 5.5–8.5 and weaker affinity for most other metal ions potentially present in the underlying paint film to minimize risk of chelation of original material (Fig. 1). Its solubility in water facilitates appropriate methods of application, whilst familiarity within the conservation profession facilitates a critical judgment of the variable parameters of deployment beyond this study. There is both a history of use for the successful treatment of lead (and zinc) soap efflorescence, having been reported as empirically more effective for this purpose than other chelating agents such as TAC, and a potential for practical use in the selected case paintings for this study. Although EDTA's affinity for a select number of other cations (notably its particularly strong affinity for iron) warrants concern, literature suggests selectivity for lead might be increased by variation of parameters, namely pH. Conditional stability constants indicate preferential sequestration of Pb^{2+} ions over Fe^{3+} ions at pH 6.5–11. Given the prevalence of iron oxide pigments in paint films it was deemed critical to test this variable in order to provide guidelines for the safe use of EDTA on oil paint films.

Analytical Materials and Methods

Testing Materials and Approaches

Test surfaces were commercially-prepared, acrylic-primed canvases, to which a thin, even layer of Raw Sienna oil paint had been applied by brush in 2009. The paint films were completely cured, though remained flexible. With the exception of a

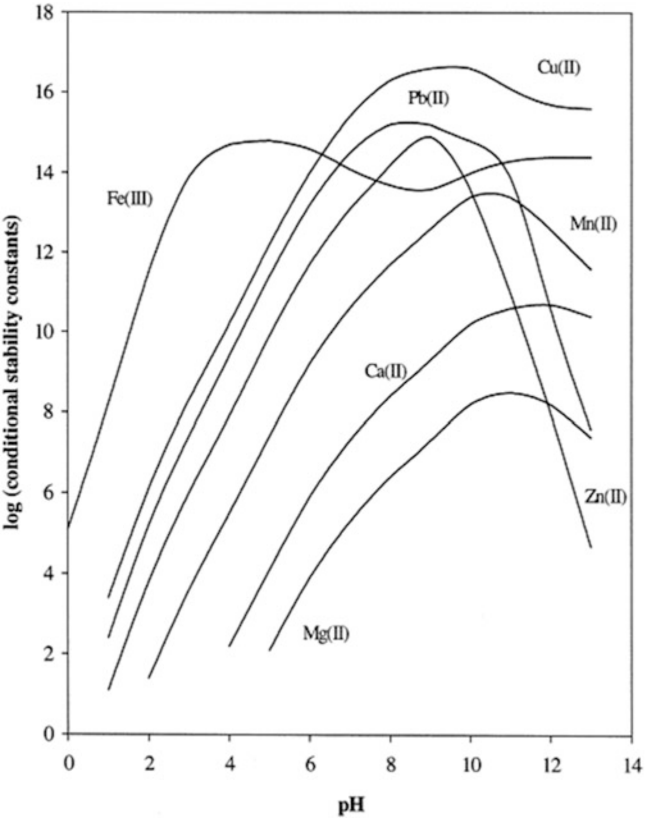

Fig. 1 Conditional stability constants of metal-EDTA complexes (Kim et al. 2003)

control surface, a layer of lead stearate was applied to the substrates, simulating the agglomeration of lead soaps on the surface of paintings. A total of six surfaces were prepared, four of which were judged as useful simulations of the intimate integration of the lead soaps with the paint film; (1) pressing the lead stearates onto the surface, (2) application of lead stearate onto reapplied wet raw sienna paint, (3) application of lead carbonate onto reapplied wet raw sienna paint and (4) application of a mixture of lead stearate and carbonate onto reapplied wet raw sienna paint.

The chelating ability of EDTA is dependent on a number of variables; EDTA is available both in its pure form and as several salts (differing in their respective solubilities and recommended for different pH ranges), the concentration of an EDTA solution determines the number of ligands available for the complexation of metal ions, the pH of a solution can optimize preference for different cations, and application methods affect the penetration of the solution, the mechanical action required and the evenness of removal. EDTA in its pure form was selected for testing, a pH range 5.5–8.5 (controlled by addition of ammonium hydroxide) was selected as appropriate for use on oil paint films, and concentrations of 2.5, 5, 7.5 and 10 % were chosen to cover the range of concentrations previously reported as effective. The solutions were applied as free solutions with a cotton swab, gelled with both low and high molecular weight methylcellulose, and gelled with Agar. Following treatment, surfaces were cleared with deionised water by swab rolling for 30 s, or in the case of areas tested with Agar gel, by a 1-min application of deionised water-Agar gel.

Efficacy of removal was assessed by a number of complimentary methods; visual observations and photomicrographs were recorded before and after treatment, SEM imaging was used to investigate the nature of the surface following treatment and the distribution of remaining lead compounds, and cross sections were compared to a reference sample to analyse the nature of the lead compound/paint layer relationship and the effect of the chelant on the iron oxide paint film.

Analytical Techniques

A HIROX digital microscope KH-7700 was used to capture full in-focus microphotographs and three-dimensional images, stacked by an algorithm determining in focus planes of a series of images (recorded at intervals) by contrast. The three-dimensional data enabled accurate measurements of surface profiles before and after cleaning. A dual illumination revolver zoom lens MXG-2500REZ with magnifications ranging from 35× to 2,500× was used and a FOBA stand used to compensate for the three-dimensionality of the objects studied. Additional photomicrographs were captured with a Leica M165C Microscope with Leica DFC 500 camera and Leica Application Suite software (Version 3.7).

SEM was undertaken at Rijksdienst voor Cultureel Erfgoed, Amsterdam (RCE) with Dr. Ineke Joosten – JEOL JSM-5910 LV Variable Pressure SEM used for SE and BSE imaging – The Natural History Museum, London (NHM) with Dr. Alex Ball – ZEISS Ultra Plus Gemini FEG used for SEI and LEO 1455 Variable Pressure SEM used for BSE – and King's College, London (KCL) – Hitachi S4000 SEM FEG used for BSE and EDX with INCA microanalysis suite.

ATR-FTIR on sample scrapings was performed using a Perkin Elmer Spectrum 1000 FT-IR combined with a GrasebySpecac Golden Gate Single Reflection Diamond ATR, from 4,000 to 400 cm^{-1} for 16 scans and a resolution of 4 cm^{-1}. ATR-FTIR on embedded cross-sections was performed using a Bio-Rad Stringray, combining the Bio-Rad FTS-6000 spectrometer equipped with a Bio-Rad UMA 500 infrared microscope with a 64×64 mercury-cadmium telluride (MCT) focal plane array camera. Analysis of the sample was carried out in reflection mode recorded with a 16 cm^{-1} spatial resolution, a step scan frequency of 1 Hz, and an UDR of 4. The reflection measurements were corrected by the Kramers-Krönig transformation.

Py-GC-MS analysis was performed using a Focus ISQ Thermo Quest mass spectrometer with a 20 m SLB5ms column, id 0.18 mm, ft 0.18 μm. One-shot

Pyrolysis at 550 °C. The inlet temperature was 300 °C, while the MS interface was at 280 °C. The temperature programme was set from 35 to 300 °C with a ramp of 10 °C/min, held isothermally for 3 min; total runtime 25 min. The MS was run in Full Scan mode (m/z 40–600) with a speed of 1.9 scans/s. Samples were derivatised with TMAH 2.5 %, using 2 internal standard (fatty acid C13 and C23) and data was processed using Xcalibur 1.4 software.

Test Results[6]

Concentration

An increase in concentration resulted in increased efficiency, with lead compounds affected faster and a greater degree of reduction achieved. Low concentrations (i.e. 2.5%w/v) resulted in a greater degree of damage to the underlying paint film, particularly when applied by swab. By reducing the quantity of EDTA available for chelation, the mechanism of removal was primarily mechanical, leading to redistribution of material over the test surface and damage of the paint film in test surfaces 2–4 where the lead compounds were more intimately bound with the substrate. The result of removal by mechanical action is evident in cross-section where craters remain as a result of dislodged material and by SEM imaging, parallel abrasion marks resulting from the rolling of the swab. A higher concentration did not consistently result in a greater degree of disruption to the paint film, the greater risk of damage to the paint substrate offset by greater efficiency, which consequently required less prolonged exposure of the paint film to the cleaning reagent, and a lesser degree of mechanical action.

pH

A higher pH led to increased efficiency both in the speed of action and the degree of reduction achieved, though it also commonly affected the paint layer beneath attested by colour removed on the swab. The resulting surface appearing rougher in SEM, the smooth organic surface layer of the medium-rich paint having been etched. However, again a more efficient removal reduced the length of application required, which could potentially offset the vulnerability of the paint film. Where the lead compounds were intimately bound with the paint surface, colour on the swab was more commonly noted for solutions of pH 5.5 than for pH 6.5, particularly in the case of lower concentrations of EDTA gelled with low molecular weight methylcellulose. Equivalent application in free solution did not consistently result in the affection of the paint substrate, and thus the detrimental affection appears due to

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[6] Comprehensive results of tests carried out can be found in (Sawicka 2013).

the chelation of Fe ions rather than mechanical action. This correlates to conditional stability constants, which indicate a preference for Fe^{3+} ions below a pH of 6.5 (Fig. 1).

Application Method

Reduction in mechanical action necessitated by the application method largely minimized the damage caused to the paint substrate. Colour removed during testing with methylcellulose gels was partly due to the mechanical action of the swab during clearance, as reflected in the results of Agar gel testing, where (with one anomaly) no effect on the paint film was recorded. The lack of mechanical action due to clearance with Agar, also facilitated an even reduction of the lead compounds, SEM images illustrating the three-dimensional surface remaining in comparison to those smoothed and flattened by the rolling of a swab. Differing viscosities of methylcellulose gel were seen to be equally as effective. However, increased viscosity, which restricted interaction of the cleaning reagent and further reduced penetration due to the increased water retention of the gel, resulted in fewer cases of damage to the paint substrate.

Practical Application

Two case studies exhibiting lead soap efflorescence were selected to further investigate the potential of EDTA to remove the inorganic surface deposits beyond the limitations of a simulated system. A variety of manifestations of the inorganic efflorescence was visible across the two paintings, providing ample opportunity to assess the viability of EDTA as a treatment option for the range that a conservator may face. Testing was guided by the conclusions drawn from the simulated surfaces and the efficacy of removal was assessed by the same means.

Case Study 1: Portrait of Pieter Jacob Teding van Berkhout

Background

Portrait of Pieter Jacob Teding van Berkhout, executed in oil on a commercially-primed, basket-weave canvas (85.2 cm × 64.3 cm), was painted by the Dutch artist Sigisbert Chrétien Bosch Reitz in 1891/1894 (Fig. 2). The painting displays a white, unevenly-distributed surface material, py-GC-MS, ATR-FTIR and SEM-EDX analysis of which indicates a composition predominantly of lead stearate, lead

Fig. 2 *Portrait of Pieter Jacob Teding van Berkhout*, Sigisbert Chrétien Bosch Reitz, 1891/1894. Before treatment

palmitate and mineralized lead soaps.[7] The material appears in a variety of forms across the painting; as patches of densely packed crystals, as fine rod-shaped crystals in the valleys of brushstrokes and as a thin haze of particulate material. Distribution and form appears uncorrelated to the painting's composition although spots of the dense crystalline material are most prevalent in the green cushion (lower left quadrant), whilst the black stockings display a more homogenous distribution of fine crystals. The paler green background appears largely unaffected although crystalline material is visible in the upper-left and lower-right corners. Indeed, the horizontal band efflorescence across the lower right, suggests that the painting was partially protected by some means (the painting was part of a stack of paintings stored in a shed for some years) rather than a particular invulnerability to efflorescence in this area. Though the distribution of efflorescence cannot be rationalised by the presence of a specific material, it does appear influenced by material composition. Crystalline material is congregated around the edges of paint passages, in the organic material along the jaw, and around a series of glossy drips in the sitter's face. Crystal growth extends over cracks in the paint film though concurrently cracks pass through the efflorescence, indicating an extended period of formation.

Examination of the efflorescing surface with electron microscopy demonstrates the superficial growth of highly-scattering, plate-like structures, accumulating

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[7] A previous technical study was carried out by Keune et al. (2007).

beneath a film of varnish. Aggregation of these lead rich shards has caused disturbance to the varnish film, undulations indicative of the three-dimensional structures beneath. Imaging of cross-sections with SEM illustrate the intimate integration of crystals within the paint surface, and the well-developed lamellar arrangements in the surface deposit, taken as an indication of remineralisation within lead soap aggregates (Keune et al. 2007).

Testing

Dense clusters of crystalline material located on the green cushion (lower left quadrant) were selected for testing of EDTA solutions, ample testing sites allowing as accurate a comparison of efficacy as possible. The surface was examined before and after cleaning with a Hirox 3D digital microscope.

Concentration

Free solutions displayed an increased efficiency with an increase in concentration. After c.50 swab rolls, solutions of 2.5 and 5 % (pH 6.5) did not result in any visible change, whilst thinning of the efflorescence was notable at higher concentrations. Despite this increased efficiency in the chelation of the lead-based efflorescence – including material lying beneath the surface of the varnish, particularly along lines of cracking – it did not appear to independently affect the metallic pigments of the paint film beneath.

pH

An increase in pH resulted in a greater degree of reduction. However, a higher pH corresponded to an incremental affection of the paint substrate. Given that no sensitivity was noted for any solutions of pH 6.5, it may be hypothesized that damage caused to the paint layer is partly due to affection of organic components at an alkaline pH, which also facilitated the increased reduction.

Application

Application of the cleaning reagent affected action and controllability. Whilst the swabbing of free solutions enabled better assessment of the surface during cleaning, an uneven removal was evident at higher magnification. Conversely, gelling solutions with methylcellulose limited mechanical action, resulting in a more even reduction (Fig. 3), and restricted penetration of the solution, which facilitated the use of solutions at a higher pH, without damage to the underlying paint film. Though Agar gel performed similarly in this respect, the efficiency of reduction

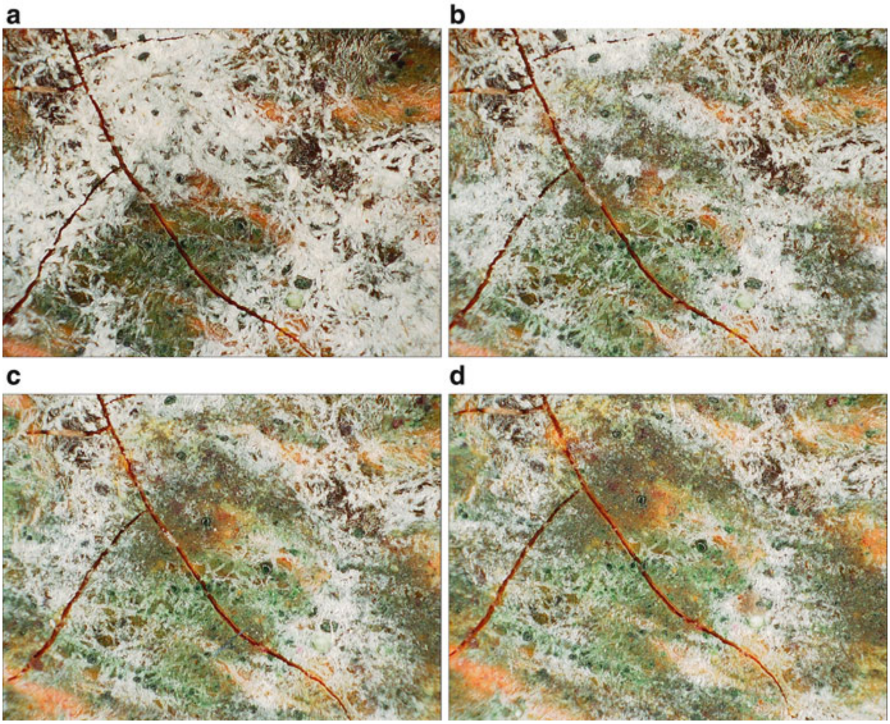

Fig. 3 Photomicrographs of lead soap efflorescence removal with MC gel, 5 % w/v EDTA, pH 6.5. (**a**) Before Cleaning; (**b**) After 30 s; (**c**) After 30 s (1 min total); (**d**) After 30 s (1.5 min total)

was reduced, requiring lengthier applications. Given the fine margin for error, it was difficult to estimate the critical point between chelation of the efflorescence and affection of the paint substrate in these prolonged applications. Shorter, repeated applications necessitated could be detrimental to the paint layers.

Evaluating the Success of Removal

Following testing, efflorescence from a site to the left of the sitter's proper right elbow was removed with a 5 % w/v solution of EDTA, pH 8.5, gelled with high molecular weight methylcellulose, applied for a total of 4 min. Visually, the surface appeared rougher than the smooth film of the surrounding varnish, though where the dense crystalline material had been located, nuances of the paint film beneath were now visible.

Examination of the treated surface in cross-section reveals a surface apparently clear of the translucent-whitish efflorescence evident in untreated samples, though ultra-violet light indicates a very thin film of the fluorescent material remains in the interstices of the rough paint surface (Fig. 4). This material is not highly scattering in

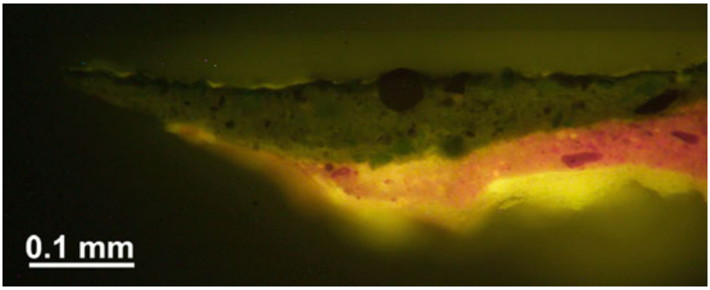

Fig. 4 Cross-section of sample taken after treatment with MC gel, 5 % w/v EDTA, pH 8.5, viewed under ultra-violet light

SEM backscatter mode, and thus it appears the lead has been successfully chelated, only the organic component remaining. Though the surface appears intact, a number of fractures are present. Whilst treatment does not seem to have initiated the cracks – present throughout the sample – it is possible the aqueous solution has exacerbated the issue. However, as the sample was divided it may be an artefact of the cleaving process.

Analysis of the treated surface with SEM reveals a fairly rough but even surface, with fine fracturing correlating to aforementioned observations. The pale surface of the sample in backscatter mode signifies the presence of a very thin film of lead-containing efflorescence with localised striations (relating to the parallel plate-like structures of the efflorescence) indicating an even and superficial thinning. Sharp-edged varnish residues suggest mechanical fracturing of the resin during treatment, though their surfaces appear unaffected, comparable to that of the intact varnish film.

Case Study 2: Return from the Front

Background

Return from the Front by the British artist Kate Elizabeth Olver c.1915, depicts a soldier returned from the front line during WW1 (Fig. 5). The painting, executed on a commercially-primed, basket-weave canvas (136.9 cm × 99.0 cm), exhibits a pale greyish surface material located predominantly over the lower third. The material is present in the interstices of the textured paint surface, as a coherent, flaky, particulate crust. Although cracks can be seen to pass cleanly through the crust, possibly indicating ageing of the paint film following its formation, the material can also be seen to accumulate around cracks, which have potentially provided transport lines for the migration of material to the surface.

Although efflorescence formation appears unattributable to distinct paint passages, some relation to the composition is highlighted by the isolated passage of

Fig. 5 *Return From the Front*, Kate Elizabeth Olver, c. 1915. Before treatment

efflorescence in the coat of the soldier, apparently demarcating the area between the soldier's underlying legs. It may thus be hypothesised that certain paint layers have facilitated or conversely inhibited the migration of efflorescence. Efflorescence appears less pronounced in areas thickly varnished, though it is unclear whether varnish has limited migration or is simply saturating efflorescence beneath. The efflorescence-free tips of the undulating paint texture also evidence a film of varnish in ultra-violet light, potentially supporting the latter theory, or alternatively suggesting that efflorescence is blocking the fluorescence of a consistent varnish film.

A combination of ATR-FTIR and py-GC-MS analysis of the superficial material suggests the presence of lead in the form of soaps. The sulphates and methane sulphonic acids detected, intimate the modification of lead soaps to an energetically-favourable mineral phase; lead sulphate. Given the presence of vermilion, the paint layers themselves present a potential source of sulphur, though given the imbibition of soot and dirt, the mineralised phase is likely formed superficially on reaction to atmospheric gases. SEM examination of an efflorescence-containing sample reveals a dense but friable crust covering the surface of the sample. It appears patchily integrated with organic medium, though largely resembles an accumulation of fine particles. The lead-containing material fluoresces with ultra-violet illumination and is strongly scattering in SEM backscatter mode, the latter illustrating the well-developed lamellar arrangements of the surface deposit and its intimate integration with the underlying paint film, with no clear interface visible.

Testing

The efflorescent crust located on the brown foreground was selected for testing of EDTA solutions, ample testing sites allowing as accurate a comparison as possible. The surface was examined before and after cleaning with a Leica M165C microscope.

Concentration

Testing free solutions of EDTA demonstrated the varying efficiency of lead chelation, increasing incrementally with an increase in concentration. Despite concern for the pigments of the underlying paint layer, concentration as an independent variable did not appear to increase the risk presented.

pH

Raising the pH of the solution resulted in increased efficiency of efflorescence removal. Although this did not necessarily affect the paint immediately beneath the crust, a pH of 7.5 and above did result in damage to the unaffected original paint film, affection exacerbated by the mechanical action of the swab. The effect was not observed in areas where a layer of varnish was present, which effectively provided a barrier against the solution.

Application

Application affected both action and controllability. Whilst swab-application of free solutions enabled a better assessment of the surface during cleaning, an uneven removal of efflorescence resulted and mechanical action of the swab caused abrasion to the vulnerable peaks of unvarnished paint. Gelling solutions with methylcellulose facilitated a more even reduction, although the mechanical action of clearance still abraded the peaks of the textured paint film when increasingly vulnerable at higher pHs. Repeated applications of gelled solutions proved more effective than a single, prolonged application and enabled better intermediary assessment of the surface, although they presented greater risk in light of the detrimental mechanical action of clearance. Agitation of the gel with a sable brush, helped to bring the efflorescent material into solution, thus providing a viable alternative.

Removal of the Varnish Layer

Removal of the efflorescence prior to the removal of vanish resulted in thin rings of the whitish surface deposit around the patches of vanish, where efflorescence and

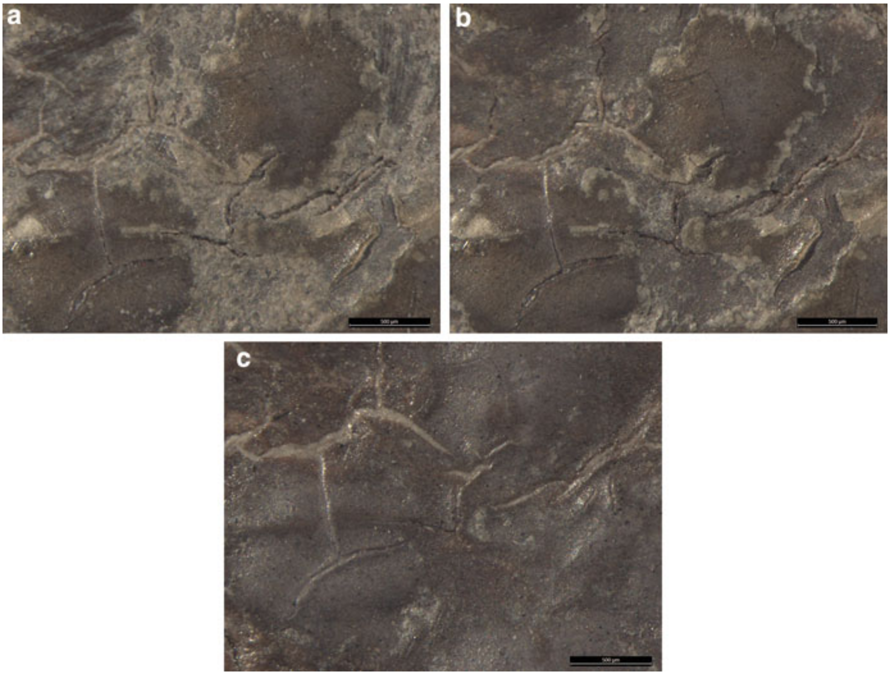

Fig. 6 Photomicrographs of lead soap efflorescence removal with MC gel, 5 % w/v EDTA, pH 6.5. (**a**) Before Cleaning; (**b**) After Cleaning (1.5 min application); (**c**) After removal of residual varnish

varnish were integrated, though these were seen to be eliminated with subsequent varnish removal (Fig. 6). Although initial varnish removal facilitated a more even reduction, residual varnish remained, necessitating further application of solvents. Given the varnish layer provided an effective barrier between paint film and cleaning solution, and that rings of residual efflorescence were cleared by the subsequent varnish removal, it was concluded that varnish should not be removed prior to treatment.

Evaluating the Success of Removal

Following testing conclusions, efflorescence from a selected site in the lower left foreground was removed with a 5 % w/v solution of EDTA, pH 6.5, gelled with high molecular weight methylcellulose, applied for a total of 2.5 min and agitated with a sable brush prior to clearance. Visually, the cleared surface appeared slightly rougher and more-light scattering than a saturated paint film, although reduction appeared very even and – with the exception of those integrated within the varnish film – very few visible residues remained.

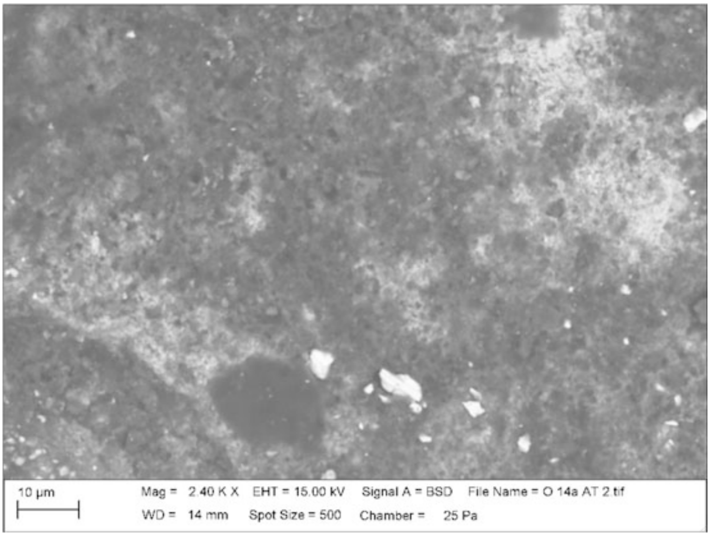

Fig. 7 Backscattered electron SEM image of sample after treatment with MC gel, 5 % w/v EDTA, pH 6.5

Microscopic examination of the treated surface in cross-section shows a thin layer of the pale greyish efflorescence, just discernable at the surface of the paint film. Ultra-violet illumination corroborates a relatively smooth and even layer, thinned just shy of the indistinct interface with the underlying paint film. Pigment particles appear partially bound within the remaining film of efflorescence and thus further thinning of the residual crust is inadvisable.

SEM analysis of the treated sample confirms the rough but fairly even surface topography. Given the intact film of efflorescence observed in cross-section, the topography likely relates to the surface of residual efflorescence as opposed disturbance of the paint film. This is corroborated by the backscatter image, which indicates thin residual efflorescence (Fig. 7). Brighter areas, indicating a greater quantity of residual efflorescence, appear partially linked to the presence of organic material remaining on the surface, which may have inhibited the access of the gel. The upper paint film appears in tact, with the underlying, pale purple layer only visible at the sheered edges. At high magnification, no residues of the gelled solution were distinguishable.

Post Treatment Recurrence of Lead Soap Efflorescence

The formation of lead soap efflorescence is influenced by both inherent material instability and environmental factors. Hypothetically therefore, the propensity for reformation of crusts after treatment may depend on both these factors, as indicated by studies that observed the common recurrence of associated phenomenon such as fatty acid bloom.[8]

It is possible that some conservation treatments may exacerbate the formation of efflorescence. Though difficult to assess, Van Loon (2008) suggested that reagents for varnish removal and surface cleaning may influence the formation of crusts and their composition, successive treatments providing the potential for a cumulative effect. Removal of the efflorescence with a chelating agent could thus impact future formation; the temporary moisture gradient set up by the aqueous cleaning method could potentially promote the migration of lead soaps. Moreover, the removal of the stable products of efflorescence may alter the equilibrium of the paint system, favoring migration to the cleaned surface.

Re-examination of two Arthur Walker paintings from the Royal Academy, which had previously undergone treatment with chelating agents to remove the visually disturbing lead soap efflorescence,[9] was carried out and the results compared to *Walker's Studio No. 1* by the same artist and *Portrait of Mrs Thorpe* by James Smetham, which had received no treatment of the superficial efflorescence. The propensity to recur was clearly demonstrated Walker's *Reclining Nude*, on which the efflorescence recurred within 4 years following its initial removal with a 2 % w/v solution of triammonium citrate. During this time the painting remained largely unvarnished, with only a thin and patchy local application over the figures and cushions (artist applied), and the painting underwent a series of flattening treatments involving exposure of the canvas to acute moisture. However following further treatment with a 2.5 % solution of ethylenediaminetetraacetic acid (pH 8.5) and the application of a synthetic varnish, no sign of recurrence was evident after a further 4 years of storage in the stable environment of the Royal Academy stores, kept at 20 °C at 50 % relative humidity. Similarly no indication of recurrence or further deterioration was identifiable on *Two Girls Reading a Book,* which was also varnished following treatment with EDTA, and *Walker's Studio No. 1* and *Portrait of Mrs Thorpe*, the efflorescence on which was dealt with through saturating with varnish and aesthetically integrated through retouching. Based on these case studies, preventive conservation measures might include considerations for environmental control and framing.

Conclusion

Identification of lead soap efflorescence is complicated by the wide range of forms it assumes. Case studies evidence manifestations varying from dense crystalline spots and thick layered crusts, to a fine haze, closely resembling that of organic

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[8] A recurring cycle of organic fatty acid bloom was noted for the Stanley Spencer paintings in Sandham Chapel (Burnstock et al. (1993)).

[9] Treatment undertaken at the department of Conservation & Technology at the Courtauld Institute of Art from 2004 to 2009.

efflorescence. The visually indistinct nature of the degradation phenomenon has caused confusion, clarification further hindered by the use of ambiguous nonenclature. As relatively few paintings exhibiting this phenomenon have been thoroughly investigated, analysis of the efflorescence has proved critical in understanding the nature of the surface product and its formation. This in turn has enabled treatment methods to be more accurately tailored to the specifics of this phenomenon.

The two contrasting case studies explored, supported by testing with simulated efflorescing paint surfaces, substantiate the viability of reduction of disfiguring efflorescence with solutions of EDTA. Regardless of the contrasting forms of efflorescence, it was found to be possible in both cases to greatly reduce the material to a thin (and consequently far less disturbing) saturatable film, without damage to the underlying paint substrate. The aims of treatment must be tempered by the limitations posed by the indistinct interface between efflorescence and paint film. In this context, the reduction, though incomplete, should be viewed as a successful resolution. Though topographical analysis of treated samples indicated a fairly rough surface, the rough and uneven surface of both the untreated efflorescence and the underlying surface of the paint film, should be taken into account. In order to achieve a smooth and even surface, it would be necessary to unevenly thin the efflorescence mechanically, unviable given the propensity of mechanical action to damage the paint substrate.

The boundary between effective removal of the efflorescence and damage to the underlying paint film is relatively small, and hinges on a careful balance between the tested variables of concentration, pH and application. Test surfaces proved particularly useful despite the limitations of simulated testing, given the compositional similarity of the surface to the case studies, and consequently the conclusions drawn were borne true with practical testing. It was noted that mechanical action should be minimised, that concentration did not appear to independently affect the paint substrate and that a pH raised above 6.5 increased the efficiency of removal though simultaneously increased the vulnerability of the underlying paint. Gelling solutions of EDTA with methylcellulose proved effective in both limiting mechanical action and restricting penetration, whilst still facilitating critical judgement of when the desired level of reduction had been achieved. The mechanical action of clearance proved potentially damaging, though the risk was significantly reduced in comparison to the repetitive swab rolling of free solutions.

Practical testing highlighted the difficulties of judgement in the process of reduction. Due to the obscuring nature of some efflorescent crusts, the conservator must rely on inference as to the appearance of the original material they are attempting to reveal. However, comfort should be taken from the fact that analysis of the surface after treatment simply corroborated visual observations and thus reliance on good observational skills, due caution and the ability to make critical judgements should serve the conservator well. Following removal of the efflorescence, which does not appear to aggravate the inherent instabilities of the painting structure, recurrence of the phenomenon may be at least be stalled by maintenance of a stable environment, limiting exposure to moisture, and varnishing the painting where considered appropriate. Treatment with EDTA, with variables tailored to the specificities of the individual painting, thus offers a viable resolution to the issue of the visually disturbing aggregates, crusts and hazes of lead soap efflorescence.

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