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Georges Seurat, *Bathers at Asnières* (NG 3908),
detail of PLATE 4, page 7

TITLE PAGE
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detail of PLATE 1, page 38

Pigment-medium Interactions in Oil Paint Films containing Red Lead or Lead-tin Yellow

CATHERINE HIGGITT, MARIKA SPRING AND DAVID SAUNDERS

During the routine examination of paintings, translucent white lumps or inclusions are often observed in oil paints containing red lead or lead-tin yellow 'type I'. These lumps vary in size, but are usually most easily visible under the microscope, either in cross-sections of paint samples or on the paint surface. In some cases – for example in the *Portrait of Don Andrés del Peral* by Francisco de Goya (NG 1951, PLATE 1) – they are large enough to be seen with the naked eye. In this painting the lumps are in the ground layer (which contains red lead) but are so large that they protrude through the paint layers and above the surface, giving the whole painting a pronounced gritty texture. They are visible in the X-radiograph of the painting as small white dots (FIG. 1).

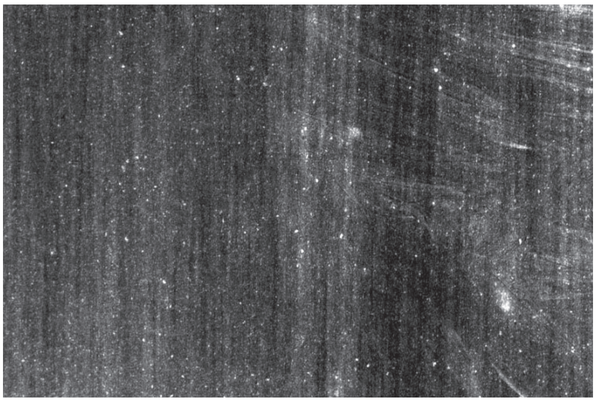

FIG. 1 Francisco de Goya, *Portrait of Don Andrés del Peral* (NG 1951). Detail of X-radiograph in which the inclusions are visible as small white dots.

PLATE 1 Francisco de Goya, *Portrait of Don Andrés del Peral* (NG 1951), before 1798. Poplar, 95 × 65.7 cm.

The same phenomenon has also been observed in samples from wall paintings executed in an oil medium.[1] However, the extremely damp environmental conditions to which wall paintings are often subjected can also lead to a more dramatic lightening of red lead-containing paint films due to conversion to lead carbonate, not only in oil but in a variety of binding media.[2] This related, but mechanistically different, deterioration process is the subject of a separate investigation.[3]

Inclusions have been noted in descriptions of paint samples published as early as the 1970s.[4] They have variously been interpreted as interstices or 'bubbles' within the film, resulting from the use of an aqueous binding medium such as egg tempera, or as indicative of the use of a mixed medium or emulsion (with the inclusions being protein or other non-glyceride material).[5] It has also been suggested that the lumps are a coarse grade of lead white deliberately added to the paint to give it texture.[6] It is only relatively recently, with the advent of Fourier transform infrared (FTIR) microscopy, that it has been possible to analyse them reliably. A number of studies have been published.[7] These include Plahter

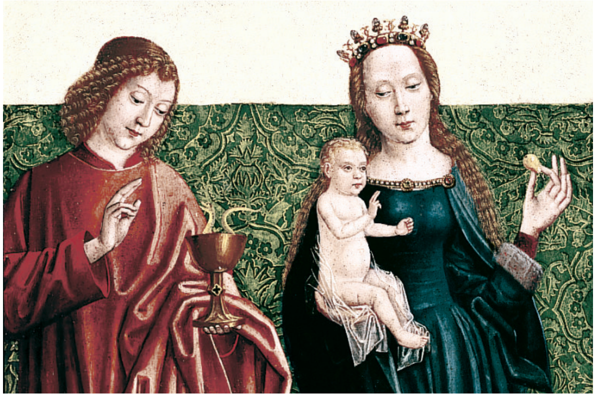

PLATE 2a Detail of *The Virgin and Child with Saint John*, German, 16th century, on the reverse of *Saints Peter and Dorothy* (NG 707), by the Master of the Saint Bartholomew Altarpiece, probably 1505–10. Oak, 125.7 × 71.1 cm.

and White's FTIR analysis of inclusions in the ground of *The Young Christ among the Doctors* by Teodoer van Baburen (Nasjonalgalleriet, Oslo),[8] White's analysis of a lead-tin yellow-containing paint from *William Feilding, 1st Earl of Denbigh* by Van Dyck (NG 5633)[9] and analysis by Noble et al. of Rembrandt's *Anatomy Lesson of Dr Nicolaes Tulp* (Mauritshuis, The Hague).[10] The common conclusion of these analyses was that the inclusions contain lead carbonate and lead carboxylates (lead fatty acid soaps) formed by reaction of the pigment with the oil medium.

The above analyses relate to Northern European seventeenth-century paintings. The phenomenon is not, however, confined to this period, but is ubiquitous in oil paintings from all over Europe during the period in which red lead and lead-tin yellow 'type I'

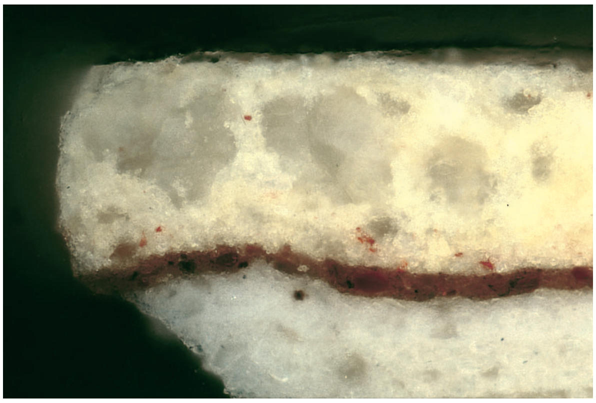

PLATE 2b Cross-section from the reverse of NG 707; highlight of the Virgin's crown. Large translucent white inclusions are visible within the lead-tin yellow paint layer. Original magnification 500×; actual magnification 440×.

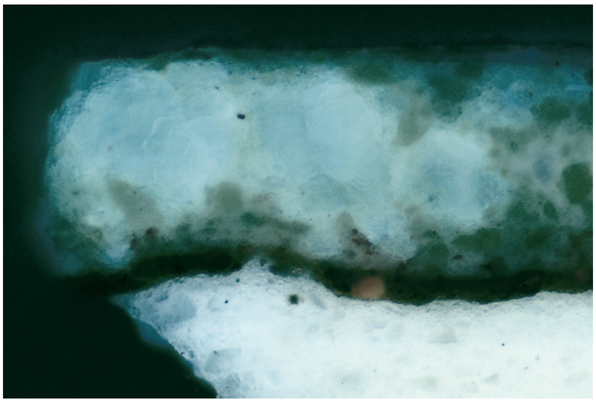

PLATE 2c Cross-section from the reverse of NG 707; highlight of the Virgin's crown, ultraviolet light. Original magnification 500×; actual magnification 440×.

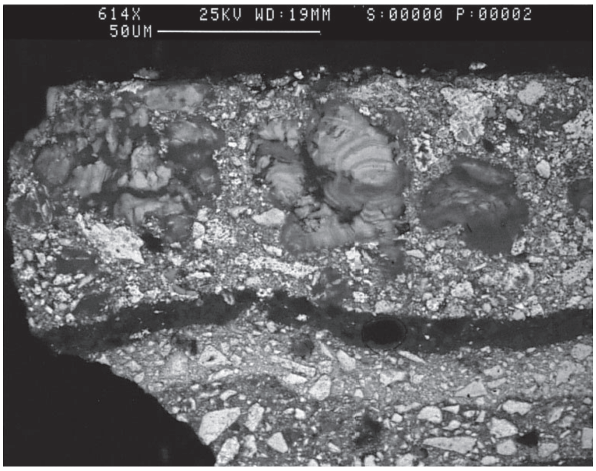

FIG. 2a Reverse of NG 707. Back-scattered electron image of the cross-section from the Virgin's crown (shown in PLATES 2b and c).

FIG. 2b Detail of the back-scattered image in FIG. 2a.

were used as pigments. Here, we present detailed analyses of inclusions in works ranging in date from the thirteenth to the eighteenth centuries. In addition, the records of examination of cross-sections held in the Scientific Department of the National Gallery (which date back to the 1950s) confirm that these inclusions are common in paint films containing a significant proportion of red lead or lead-tin yellow. Analysis of samples from some thirty-five of these paintings was carried out by optical microscopy, energy dispersive X-ray analysis (EDX) in the scanning electron microscope (SEM), X-ray diffraction (XRD), FTIR microscopy and gas chromatography–mass spectrometry (GC–MS). Here the results of the analysis of a larger group of paintings showing this phenomenon than has previously been examined are presented, to provide a broader view of the occurrence of lead soap inclusions and hence a deeper understanding of the mechanism and consequences of their formation. The paintings, and a summary of the results, are listed in Table 1.

Microscopic appearance of the inclusions

PLATE 2b shows a cross-section of a sample from a painting of *The Virgin and Child with Saint John* by an unknown sixteenth-century German painter (PLATE 2a), on the reverse of *Saints Peter and Dorothy* (NG 707) by the Master of the Saint Bartholomew Altarpiece. Rounded white opalescent inclusions between 30 and 50 microns in size are visible in a yellow paint layer containing only lead-tin yellow of the ‘type I’ form. The inclusions are fluorescent under ultraviolet light and can be seen to be inhomogeneous, as there is variation in the strength of the fluorescence within the inclusion, distinguishing them from ordinary coarse particles of lead white (PLATE 2c). This inhomogeneity is even clearer in the back-scattered image in the SEM (FIGS 2a and 2b). There are highly scattering (lighter grey) lead-rich regions with a lamellar structure, mostly towards the centre of the inclusions, surrounded by less scattering areas that correspond to the regions which fluoresce more strongly under ultraviolet light. These regions relate to a rather more subtle variation in translucency that is visible under normal light (PLATE 2b). EDX analysis in the SEM detected only lead in the inclusions.

Large white inclusions were also observed in the red paint of Saint Hippolytus’ hose (a mixture of vermilion and red lead) in Moretto’s *Virgin and Child with Saints* (NG 1165) of *c.*1538–40 (PLATES 3a and 3b). The inclusions have the same characteristic appearance under ultraviolet light (PLATE 3c), and in the SEM as in the lead-tin yellow paint of the Virgin’s crown in the painting of the Virgin and Saint John discussed above, but here the presence of red lead in the paint layer is responsible for their formation. The descriptions of the samples illustrated in PLATES 2 and 3 are typical of all those examined in this study.

Lead soap inclusions are quite commonly seen in the red ground layers of seventeenth-century Dutch paintings, which often contain some red lead (as a drier) mixed with red earth pigment (see Table 1). An example of this was observed on a painting by Bartholomeus van Bassen (*An Imaginary Church*, Brighton Museum and Art Gallery). In a cross-section from this painting illustrated in PLATE 4, one particularly large inclusion is visible in the red ground layer, which has erupted through the upper layers of paint. Unreacted red lead particles

PLATE 3a Moretto da Brescia, *The Madonna and Child with Saints Hippolytus and Catherine of Alexandria* (NG 1165), *c.*1538–40. Canvas, 229.2 × 135.8 cm.

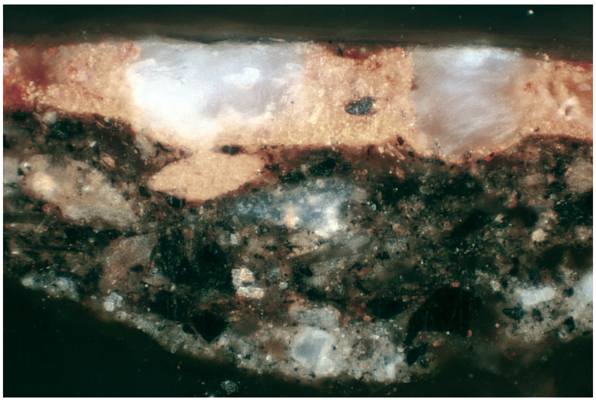

PLATE 3b Moretto da Brescia, *The Madonna and Child with Saints Hippolytus and Catherine of Alexandria*. Cross-section from the red hose of Saint Hippolytus. Two large white inclusions can be seen in the uppermost red layer, which contains red lead and vermilion. Original magnification 400×; actual magnification 350×.

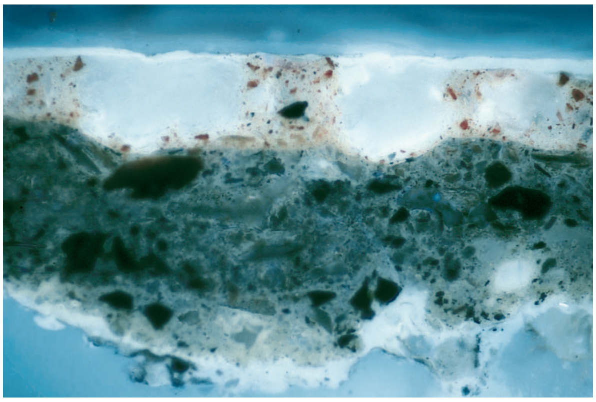

PLATE 3c Moretto da Brescia, *The Madonna and Child with Saints Hippolytus and Catherine of Alexandria*. Cross-section from the red hose of Saint Hippolytus, ultraviolet light. Original magnification 400×; actual magnification 350×.

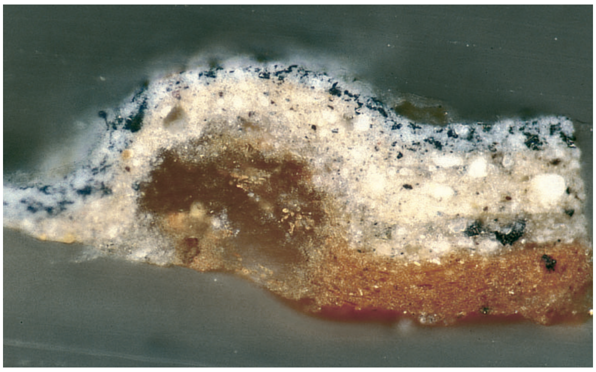

PLATE 4 Bartholomeus van Bassen, *An Imaginary Church*, 1627. Brighton Museum and Art Gallery. Cross-section from the brown foreground. The lower red ground layer contains red earth and red lead, over which is a second brownish-grey ground layer (lead white, black, brown and red lead). A very large inclusion originating in the lower red ground layer is visible. Original magnification 280×; actual magnification 275×.

surround the white translucent pustule. The painting is on panel and so the gritty texture caused by the inclusions is particularly evident on an otherwise smooth surface. Another painting in which lead soap inclusions were observed in the red ground layer (a mixture of red lead and red earth) is the *Portrait of Charles I* by Daniel Mytens (Royal Collection). Like the painting by van Bassen, the white translucent inclusions are embedded in a matrix of red earth pigment, but have unreacted red lead around them from which they originate (PLATE 5). Again, as is often the case, the growth of the inclusion has distorted the surrounding paint layers and ruptured the surface of the film. The lamellar structure that is frequently seen in inclusions is particularly well developed in this sample (FIG. 3).

Red lead is also often a component of oil mordants used for gilding, again because of its ability to aid the drying of oil. Several examples of inclusions in this type of mordant are listed in Table 1. These include the gilding on Pilate's robe in *Christ before Pilate* (NG 2154) by the Master of Cappenberg, and the gilded decoration on the canopy of the early English *Thornham Parva Retable* (St Mary's Church, Thornham Parva).

The *Westminster Retable*, which was painted in England in the thirteenth century, is the earliest painting in which inclusions have been observed. Relatively small white lumps have formed in the red lead paint of the orange lining of Saint John's cloak (PLATE 6). Since early English paintings on both panel and wall were frequently executed in oil, and often contain red lead, this is not an isolated example; several others in works from this period are listed in Table 1.[11]

We have not attempted to cover nineteenth- and twentieth-century examples of this phenomenon; the latest painting in this study, Goya's *Don Andrés del Peral* (NG 1951), dates from the last decade of the eighteenth century. The inclusions in the ground layer of this painting are around 200 microns at their largest and so, as mentioned earlier, are visible with the naked eye. They are more opaque in appearance than the previous examples illustrated, but the characteristic fluorescence and inhomogeneity are still visible in ultraviolet light (PLATES 7a and b, and FIG. 4).

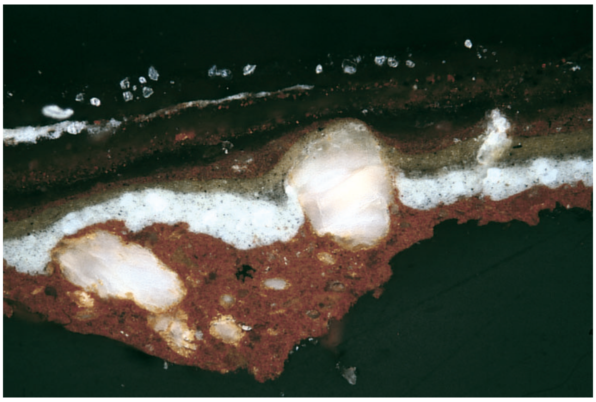

PLATE 5 Daniel Mytens, *Portrait of Charles I*, 1628. Royal Collection. Cross-section from a red drapery in the background, showing the large lead soap inclusions in the red ground layer (red earth, red lead and a little black). Unreacted red lead is visible around the white inclusions. Original magnification 200×; actual magnification 175×.

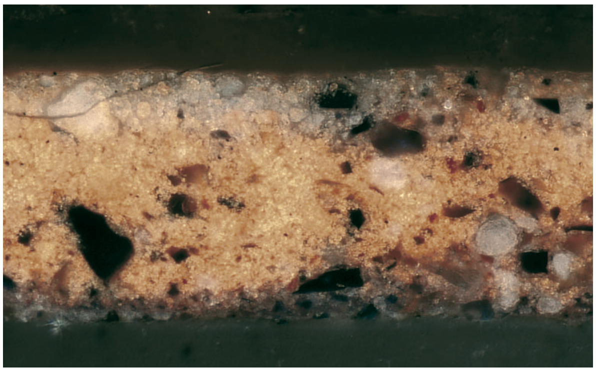

PLATE 6 English School, *The Westminster Retable* (Scene IIIa), *c.*1260–80. Westminster Abbey. Cross-section from the orange lining of Saint John's robe, showing small white relatively homogeneous inclusions within the red lead paint layer. Original magnification 500×; actual magnification 440×.

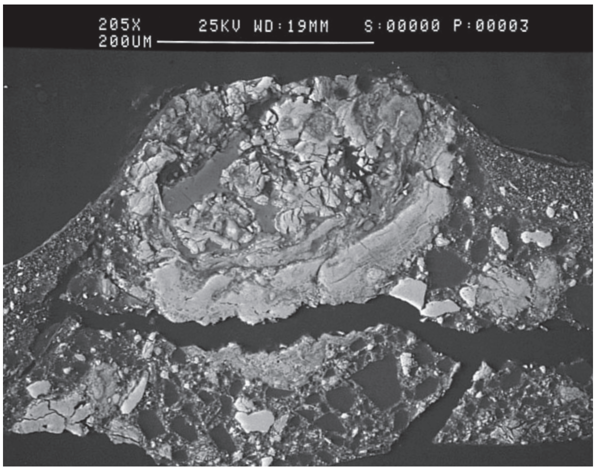

FIG. 4 Francisco de Goya, *Portrait of Don Andrés del Peral* (NG 1951). Back-scattered electron image, paint cross-section from the black background, illustrated in PLATES 7a and b.

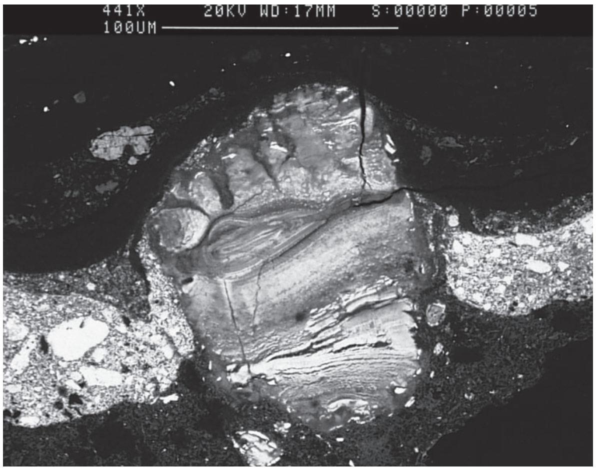

FIG. 3 Back-scattered electron image of the large pustule in the cross-section in PLATE 5, showing the pattern of precipitation of lead carbonate within an inclusion.

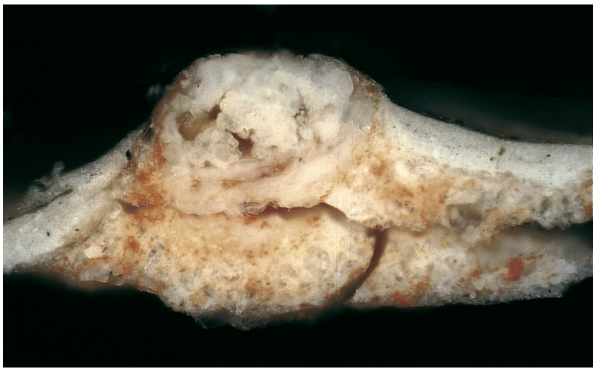

PLATE 7a Francisco de Goya, *Portrait of Don Andrés del Peral* (NG 1951), before 1798. Cross-section from the black background. The pale orange ground layer contains red lead, lead white and silica. A large relatively opaque inclusion which has broken through the upper layers of paint can be seen in the middle of the sample. Original magnification 126×; actual magnification 110×.

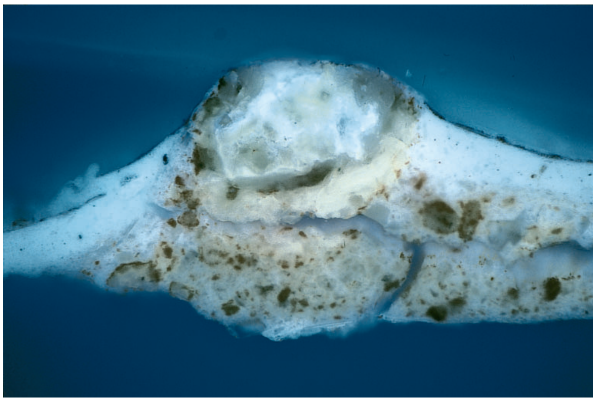

PLATE 7b Francisco de Goya, *Portrait of Don Andrés del Peral*. Cross-section from the black background, ultraviolet light. Original magnification 126×; actual magnification 110×.

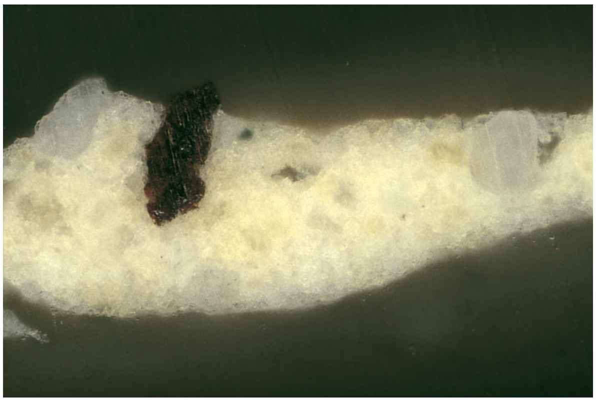

PLATE 8 Meindert Hobbema, *The Avenue at Middelharnis* (NG 830), 1689. Cross-section from the lead-tin yellow highlight of the small tree in sunlight, showing relatively homogeneous inclusions. Original magnification 500×; actual magnification 440×.

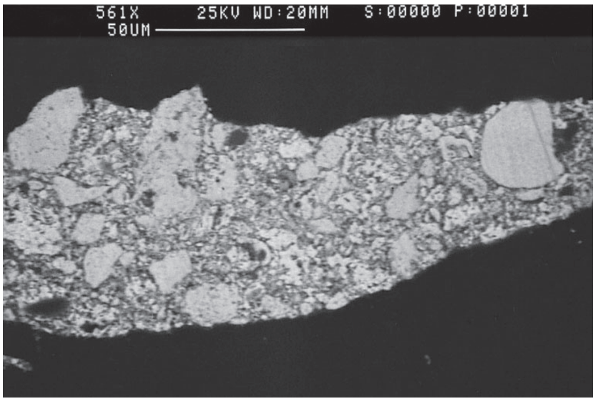

FIG. 6 Meindert Hobbema, *The Avenue at Middelharnis* (NG 830), 1689. Back-scattered electron image of the cross-section shown in PLATE 8, in which the inclusions appear relatively homogeneous.

Analysis of the inclusions

FTIR microscopy

The results of FTIR analysis of the samples listed in Table 1 are remarkably consistent, showing that the composition of the inclusions is very similar in all the examples studied. In every case they were found to comprise lead carboxylates (lead fatty acid soaps) and lead carbonate (in the basic and/or neutral form). Using a FTIR microscope and a micro compression diamond cell, it was possible to obtain good-quality transmission spectra of the inclusions. The lead soaps were identified by comparison with the literature and standards of various lead soaps prepared in the laboratory (see Appendix, p.94).[12]

The upper trace in FIG. 5 shows the infrared spectrum of an inclusion in a lead-tin yellow highlight in *The Avenue at Middelharnis* by Meindert Hobbema (NG 830). For comparison, the middle and lower traces show spectra for standards of lead palmitate and lead stearate prepared in the laboratory (see Table 2 in the Appendix). Palmitic and stearic acids are the major monocarboxylic fatty acid components of aged drying oils.[13] The strong, sharp bands at 2918 and 2849 cm^{-1} correspond to the C–H stretches of the fatty acid portion of the lead soaps.[14] The asymmetric carboxylate stretch of the lead fatty acid soaps appears as a doublet at *c.*1540 and 1513 cm^{-1} and the symmetric stretch at *c.*1419 cm^{-1}. The regular pattern of small peaks in

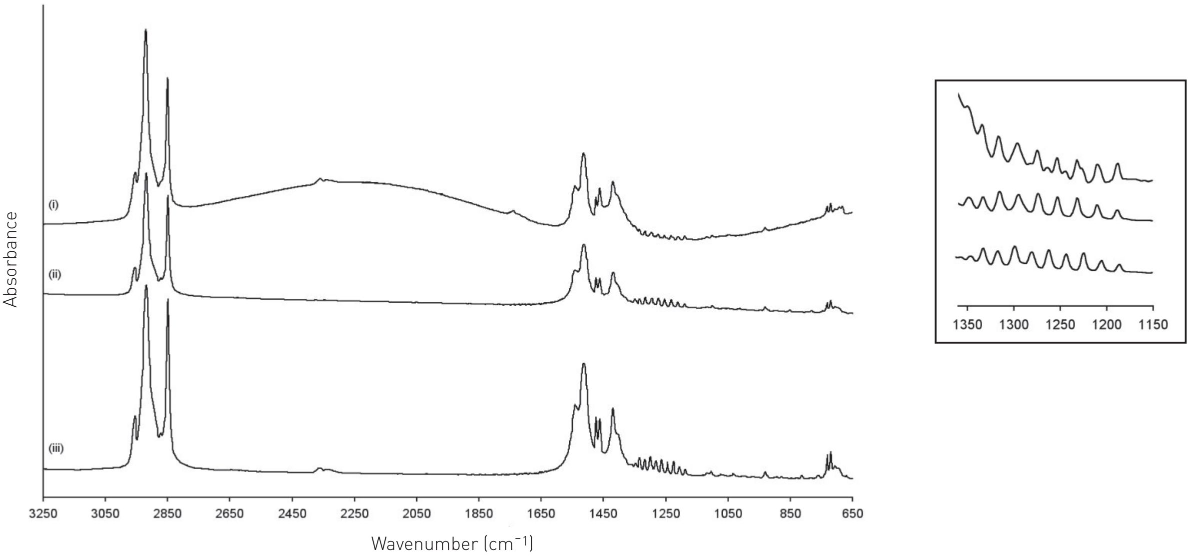

FIG. 5 FTIR spectra (3250–650 cm^{-1}) of: (i) an inclusion in the lead-tin yellow highlight on a tree from Meindert Hobbema, *The Avenue at Middelharnis* (NG 830) [upper trace]; (ii) a standard sample of lead palmitate [middle trace]; (iii) a standard sample of lead stearate [lower trace]. Inset: detail in the 1360–1150 cm^{-1} region. (The baseline roll in the upper trace is an artefact resulting from the use of a micro compression diamond cell in sample preparation.)

PLATE 9a Lorenzo Costa, *A Concert* (NG 2486), *c.*1485–95. Detail of the woman's sleeve and green bodice. The lumpy texture of the green paint is caused by inclusions in the lead-tin yellow underpaint.

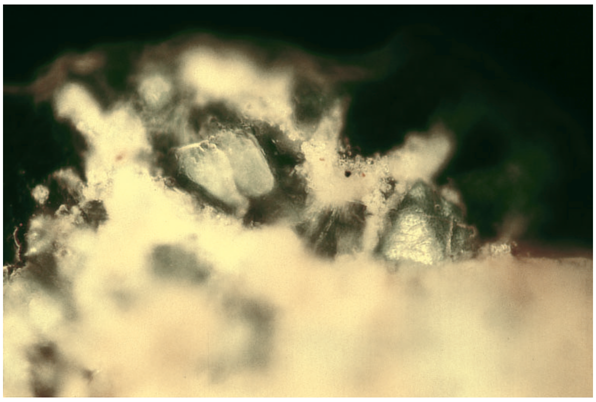

PLATE 9b Lorenzo Costa, *A Concert*. Unmounted paint fragment from a lead-tin yellow highlight on the brocade of the woman's sleeve. Translucent 'haloes' can be seen around a more opaque core in the inclusions. Original magnification 500×; actual magnification 440×.

the 1350–1180 cm^{-1} region corresponds to the vibrations associated with the long hydrocarbon chains of the fatty acids. This is an unusually clear example,[15] as the spectra are normally less well resolved and are complicated by peaks from other components such as lead carbonate and the oil binding medium. In this sample the inclusions contain less lead carbonate than many of the other examples. This is reflected in their more homogeneous appearance in normal light (PLATE 8) and in the back-scattered image in the SEM (FIG. 6).

There was some indication from the FTIR spectra that the amount of lead carbonate in the inclusions is variable, as might be expected given the variation in translucency observed in cross-sections under the microscope. The pustule in the cross-section from the painting by Goya (PLATES 7a and 7b) seems to have a particularly high proportion of lead carbonate and is relatively opaque in comparison with the inclusions in the cross-section from Hobbema's painting (PLATE 8). The distribution of the components in the inclusions was investigated by FTIR microscopy on a sample of lead-tin yellow paint from Lorenzo Costa's *A Concert* (NG 2486), where the inclusions are relatively large (PLATE 9a). The inclusion analysed has a fairly opaque centre with a halo which is more translucent and which also fluoresces more strongly in ultraviolet light (PLATE 9b). Although the infrared bands for lead carboxylates and lead carbonates overlap in the

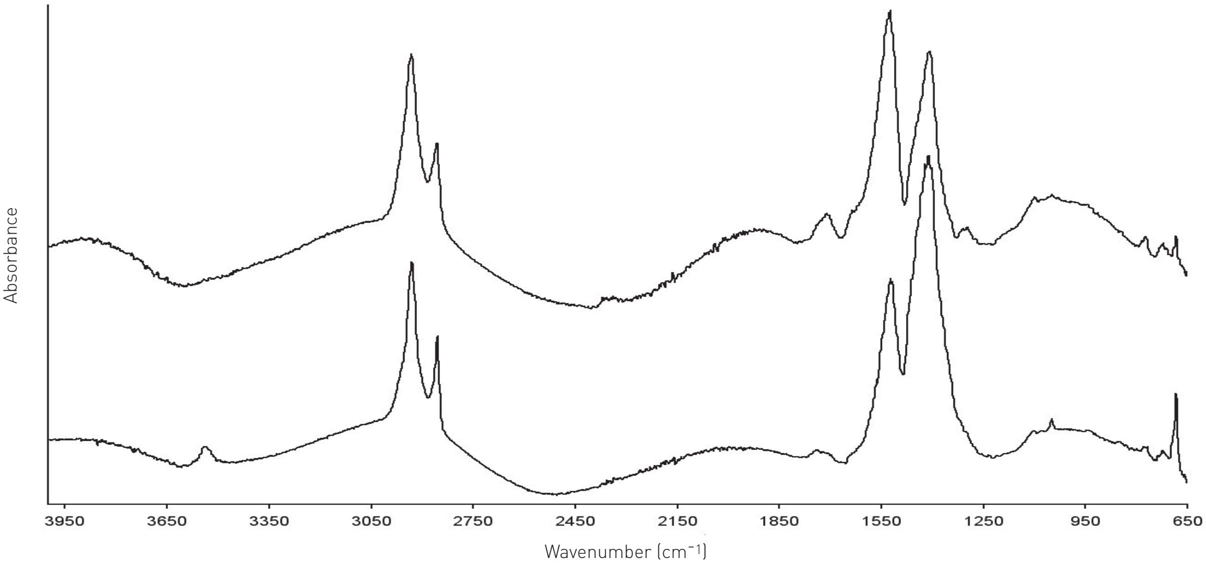

FIG. 7 Lorenzo Costa, *A Concert* (NG 2486). FTIR spectra (4000–650 cm^{-1}) from the inclusion illustrated in PLATE 9b. Upper trace: spectrum from the translucent 'halo' around the inclusion, which has a high proportion of lead-fatty acid soaps. Lower trace: spectrum from the more opaque centre of the inclusion, which has a high proportion of lead carbonate. (The baseline roll in the spectra is an artefact resulting from the use of a micro compression diamond cell in sample preparation.)

1400 cm^{-1} region, the ratio of the peaks at *c.*1400 and *c.*1500 cm^{-1} indicate that the haloes are rich in lead fatty acid soaps (FIG. 7, upper trace) and that the more opaque centres of the inclusions are rich in lead carbonate (FIG. 7, lower trace). This is consistent with the observation that the centre of the inclusion is more highly scattering (that is, lead-rich) in the back-scattered image in the SEM. Bands at 3535, 1400, 1045 and 682 cm^{-1} demonstrate that the lead carbonate in Costa's *A Concert* is present in the basic or hydrocerussite form, $2PbCO_3{\cdot}Pb(OH)_2$. The results of FTIR microscopy and XRD (see Table 1) show that this was the case in the majority of the samples examined in this study.

As will be described later, unexpectedly low levels of the dicarboxylic acid, azelaic acid (an autoxidation product of drying oils), have often been detected by GC–MS in paint films that contain inclusions. Azelaic acid is usually found in significant amounts in aged oil paint films, and is capable of forming lead soaps (see Appendix). All three of the lead soaps studied here (palmitate, stearate and azelate) can be distinguished when pure, but in the presence of the oil medium and lead pigments, it is very difficult to tell by FTIR alone precisely which lead soaps are present.[16] It is particularly hard to distinguish lead palmitate from lead stearate,[17] but the FTIR spectrum of pure lead azelate is rather different (see Table 2). As a result, if lead azelate is present it should, in some cases, be possible to detect it in a mixture of these three lead soaps. For example, in the very clear infrared spectrum obtained for the inclusion in the lead-tin yellow highlight in the Hobbema (upper trace, FIG. 5), the absence of lead azelate and the presence of a mixture of lead palmitate and stearate can readily be seen.[18]

GC–MS Analysis

Thermally assisted transmethylation GC–MS was used to investigate the presence of fatty acids and any dicarboxylic acids (produced by oxidative degradation) in the inclusions and surrounding material. The method employed here allowed all of the mono- and dicarboxylic fatty acids to be detected at once, whether they are present as free acids, as esters (glycerides) or as metal salts (soaps).[19] Analysis of inclusions separated from the bulk of the paint layer indicated that they contain palmitic and stearic acids (or their derivatives), and that this was consistent over all the samples in which the inclusions were large enough to analyse in this way. Although palmitate and stearate were found in the ratio expected for the bulk oil medium (by comparison with samples from elsewhere in the same painting), generally very little azelaic acid (or its derivatives) was found in the inclusions. This finding is consistent with the FTIR spectra where there was no obvious sign of the presence of lead azelate.

In some of the samples, where inclusions form a large part of the paint layer, the whole sample also shows a reduced azelaic acid content (see Table 1). The discovery that the presence of lead soap inclusions can have this effect on the fatty acid ratios measured by gas chromatography (GC) is of particular interest and significance, since a low azelate to palmitate ratio is characteristic of egg fats.[20] On this basis, some previous analyses of the binding medium of red lead-containing paint films (before the era of FTIR microscopy) concluded that the binding medium was egg yolk. The red lead-containing paint from the wall paintings originally in St Stephen's Chapel, Westminster, listed in Table 1, which was previously analysed with GC, is an example.[21] If the binding medium is indeed egg yolk it must, of course, contain protein, which can now be detected using FTIR microscopy. Recent re-examination by the authors of the sample from the St Stephen's Chapel wall painting using FTIR microscopy indicated that there was no evidence for the presence of amide bands (at *c.*3290, 1658, 1633 and 1550 cm^{-1}), which would be seen if proteins were present.[22] Instead, the large translucent inclusions seen in the red lead paint under the microscope yielded bands associated with lead soaps and basic lead carbonate. The binding medium of the paint in the samples from the St Stephen's Chapel wall painting is therefore oil. Every example listed in Table 1 where GC–MS gave a low azelate to palmitate ratio was also analysed by FTIR microscopy to check for the presence of protein, but none was found. The low azelate level must therefore be an effect associated with the red lead and lead-tin yellow pigments in these samples.

The 'low azelate effect' has been partly responsible for the idea that the inclusions are globules of protein, a theory that emerged from early attempts to analyse them in lead-tin yellow paints from Early Netherlandish paintings. Also perhaps responsible for this idea is the unfortunate coincidence that when cross-sections containing lead fatty acid soaps are treated with stains specific for proteins (such as amido black) they appear to give false positive results.[23] In addition, the fluorescence of the lead soap inclusions has in the past been interpreted as indicative of the presence of protein.[24]

Discussion

Examination of a large number of paintings makes it clear that inclusions are found in paint layers containing red lead or lead-tin yellow, or both. The results of analysis listed in Table 1 show that, in each case, the components of the inclusions are lead fatty acid soaps and lead carbonate, as has been found in previous studies. They are formed as a result of the reaction of a lead-containing pigment with the oil binding medium.

Red lead in linseed oil has been extensively studied because of its use as a corrosion-inhibiting paint for iron.[25] It has therefore long been known that lead(II) ions in red lead react with the fatty acids in linseed oil to form lead soaps. Red lead and lead-tin yellow 'type I' have very similar structures, so it is not surprising to find that the lead(II) ions in lead-tin yellow are also capable of reacting with oil to form lead soaps. Red lead (Pb_3O_4) has a structure with chains of lead(IV) ions, where each lead ion is surrounded by six oxygen atoms in an octahedral arrangement. The octahedra are joined by tetrahedrally coordinated lead(II) ions. In lead-tin yellow 'type I' (Pb_2SnO_4), Sn(IV) substitutes for Pb(IV) in the octahedra.[26] Dunn, reporting on the reactivity of lead pigments with oil, notes that 'red lead appeared to form the most soap, white lead a smaller amount, and chromated red lead the least amount'.[27] These results correlate with the reported availability of lead(II) ions in solution from corrosion inhibition studies.[28] This lower reactivity might explain why we have not, as yet, observed lead fatty acid soap inclusions in lead white-containing paint layers, although it is clear from FTIR spectra of samples of lead white paint from old master paintings that some lead carboxylate is formed.[29]

The component of the paint that is responsible for lead soap formation is not always immediately obvious. It may not be the major constituent of the mixture, or the only lead-containing species present. In Francisco Zurbarán's painting of *A Cup of Water and a Rose on a Silver Plate* (NG 6566), the off-white paint of the cup has a lumpy texture that is visible to the naked eye, which FTIR analysis confirmed is due to lead soap inclusions. The major component of the paint is lead white, but it also contains some lead-tin yellow, yellow earth and black. There are more inclusions in the warm grey shadows of the cup than in the whiter highlights, which suggests that it is the lead-tin yellow, rather than the lead white, that is responsible for the formation of the inclusions in this case. Lead soap inclusions embedded in a paint layer containing predominantly lead white were also seen in samples from Karel Dujardin's *Portrait of a Young Man (Self Portrait?)* (NG 1680). The fourth paint layer from the bottom in the cross-section illustrated in PLATE 10 consists of lead white, a coarse black pigment and red lead, which surrounds translucent inclusions of lead soaps. It is clear that here the lead soaps have formed from red lead, both because of the location of the soap inclusions in the layer, and because in the same cross-section there is another layer (the upper part of the double ground) consisting of lead white and coarse black, but without red lead and without lead soap inclusions. In *An Imaginary Church* by Bartolomeus van Bassen, discussed above, there are inclusions in the second ground layer, which is based on lead white, as well as in the first red ground layer (PLATES 4, 11a and 11b). In the lower ground layer, although some lead carbonate is now present inside the inclusions, lead white did not form part of the paint mixture. The lead soaps originate from the red lead seen around the perimeter of the pustules. The inclusions in the second ground layer are identical in appearance, with red lead particles around them, indicating that they also originate from red lead rather than lead white.[30]

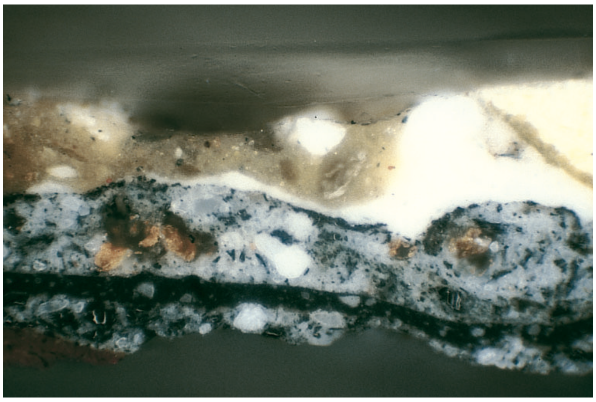

PLATE 10 Karel Dujardin, *Portrait of a Young Man (Self Portrait?)* (NG 1680), *c.*1655. Cross-section from the yellow brocade on the edge of the coat. Translucent inclusions of lead soap, surrounded by red lead particles, can be seen in the fourth paint layer (consisting of lead white, a coarse black pigment and red lead). By contrast, the second paint layer, which contains only lead white and a coarse black pigment, does not show lead soap inclusions. Original magnification 126×; actual magnification 110×.

By the nineteenth century, when the use of red lead was much reduced and lead-tin yellow had become obsolete, a large number of other lead-containing materials were being added to paint, primarily to improve its handling or drying

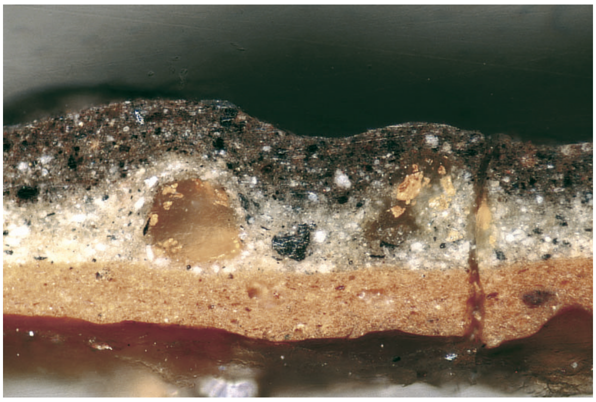

PLATE 11a Bartholomeus van Bassen, *An Imaginary Church,* 1627. Brighton Museum and Art Gallery. Cross-section from the brown foreground, showing large inclusions surrounded by red lead particles in the grey-brown second ground layer (lead white, black, brown and red lead). Original magnification 200×; actual magnification 175×.

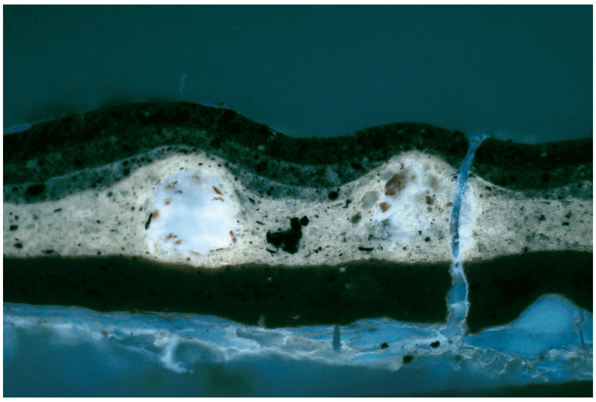

PLATE 11b Bartholomeus van Bassen, *An Imaginary Church.* Cross-section from the brown foreground, ultraviolet light. The deformation of the three dark brown paint layers over the large inclusion in the grey-brown second ground layer can be seen clearly. Original magnification 200×; actual magnification 175×.

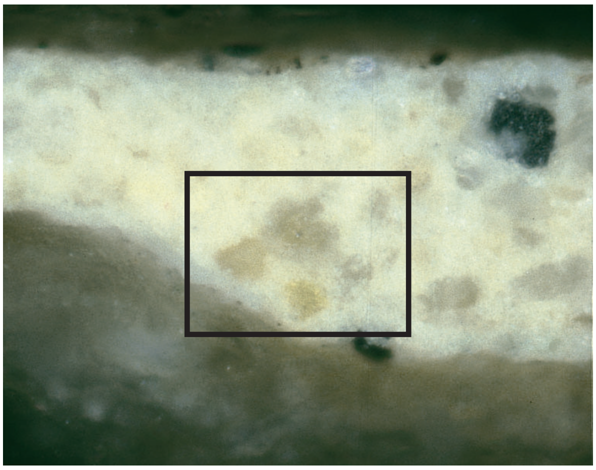

PLATE 12 Raphael, *Saint Catherine of Alexandria* (NG 168), *c.*1507–8. Cross-section from the yellow sunlit sky. Acid yellow tin-rich regions can be seen next to inclusions in the lead-tin yellow paint. Original magnification 400×; actual magnification 560×.

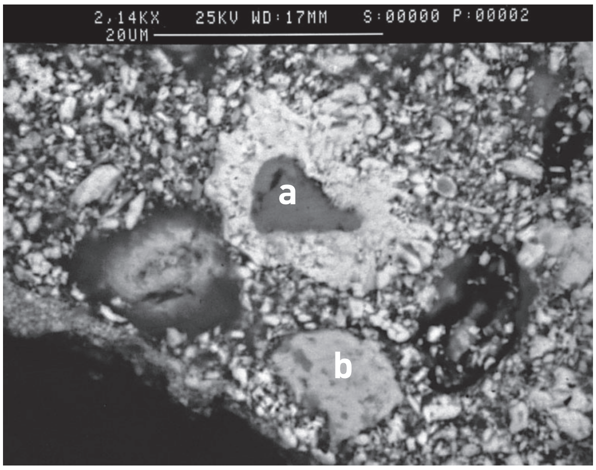

FIG. 8 Raphael, *Saint Catherine of Alexandria* (NG 168). Back-scattered electron image of a small area of the cross-section shown in PLATE 12 (marked with a box). Only tin was detected by EDX in the area labelled a. Both tin and lead were detected in the area labelled b (which is acid yellow in colour, see PLATE 12), but it is richer in tin than the rest of the lead-tin yellow matrix.

properties.[31] It seems likely that most of the occurrences of lead soap inclusions observed in nineteenth- and twentieth-century paintings derive from the interaction of these, often very soluble, lead compounds with the oil medium. For example, lead acetate (sugar of lead) was added to paint layers that now show paint defects, including ground staining, blooming and inclusions.[32] Zinc-containing pigments, which had been introduced by the nineteenth century, also readily react with fatty acids to form zinc soaps.[33]

The precise mechanism of the reaction between red lead and lead-tin yellow and the oil medium is not fully understood. If the lead(II) ions in the pigment are responsible for lead soap formation, it raises the question of what happens to the rest of the pigment. In lead-tin yellow it seems clear that only the metal ions in the +2 oxidation state are reacting with the fatty acids, since only lead is found in the inclusions by EDX analysis. With more careful EDX analysis of the matrix around the inclusions, tin-rich regions were located, as well as regions where only tin was detected. These regions may have formed as a result of depletion of lead ions from the pigment during the formation of the lead soaps. The tin-rich regions have a distinctive acid-yellow colour, while the areas containing only tin appear white (PLATE 12). The location of these areas is also visible in the back-scattered image in the SEM (FIG. 8).[34]

The white, tin-containing regions in the sample, which are more translucent than lead white, are most likely a tin oxide of some kind. A tin white pigment, probably tin oxide, is referred to in several historical treatises on painting materials, including the seventeenth-century De Mayerne manuscript, where it is suggested that Van Dyck had tried it.[35] Tin oxide has also been reported in a yellow paint containing lead-tin yellow 'type I' on one of the paintings in *The Gonzaga Cycle* by Tintoretto (Munich, Alte Pinakothek). This was interpreted as an excess of tin oxide added during manufacture of the pigment, possibly deliberately, to lighten the tone.[36] The results of the EDX analysis of lead-tin yellow paints discussed above, however, seem to suggest that the tin oxide is a deterioration product. The extent to which the formation of lead soaps, lead carbonate and tin oxide, all of which are white, causes lightening of the yellow paint is difficult to assess. The acid-yellow regions that are depleted of lead (but not completely lacking in it) appear to be a stronger colour than the unchanged pigment, as far as can be judged from cross-sections viewed under the microscope, which may compensate for the white deterioration products. In any case, this effect is likely to be much more subtle than the change in texture caused by the formation of the lead soap inclusions.

For lead-tin yellow at least, the fate of the rest of the pigment seems clear, with the Sn(IV) ions remaining in the paint film as oxides or hydrated oxides. Sn(IV) compounds are relatively stable, but this is not the case for Pb(IV). Pb(IV) species are usually strong oxidising agents and are generally unstable with respect to Pb(II), except under highly oxidising or alkaline conditions.[37] Red lead-containing paints may not, therefore, behave in the same way as lead-tin yellow-containing oil paints in this respect.[38] Further study is required in this area before a reaction mechanism can be proposed.

From the analyses undertaken it is clear that most inclusions contain lead carbonate in addition to lead carboxylates. Studies conducted at the National Gallery using test films have indicated that, in the presence of carbon dioxide and under conditions of high relative humidity (70% RH or above), red lead in any binding medium can be converted to basic lead carbonate.[39] The lightening of red lead in oil due to conversion to lead carbonates has also been reported in the literature.[40] Indeed, lead carbonates (cerussite and hydrocerussite) appear to be the most thermodynamically stable species under a wide variety of conditions.[41]

It is possible that a reaction between red lead (and by analogy lead-tin yellow) and carbon dioxide is occurring in tandem with reaction of the pigment with fatty acids in the oil, yielding the lead carbonate found in the inclusions. It is also possible, however, that only lead soaps are formed initially and that these go on to react with carbon dioxide to form lead carbonate.[42] A third possibility is that the residue (probably Pb(IV)) of the red lead (after soap formation) converts to lead carbonate.[43] Obviously this has not happened in the lead-tin yellow examples, since no tin carbonate has formed. It should of course be noted that red lead and lead-tin yellow, although similar, are not chemically identical and that different reactions may be involved. In each case, carbon dioxide is required, which might diffuse into the paint layer from the atmosphere, or perhaps be generated by decarboxylation of a fatty acid or fatty acid soap.[44]

On balance, it seems likely that the lead carbonate associated with the inclusions forms via the lead soaps, because of the lamellar structure seen in some of the larger inclusions.[45] This results from the pattern of precipitation of lead carbonate within the inclusion, and is perhaps an argument in favour of the carbon dioxide being introduced by diffusion from the atmosphere.[46] The distinctive patterns (see FIGS 2b and 3) – sometimes concentric rings, or periodic bands, or a more complicated combination of the two – are very reminiscent of Liesegang patterns, which have long been observed where precipitation reactions occur in a gel.[47]

In a well-prepared oil paint film, pigment particles will be uniformly dispersed throughout the film. It might therefore be expected that metal soaps (formed by reaction between certain pigments and the medium) will also be evenly spread throughout the film.[48] However, the lead soaps we have observed in the paintings in this study have formed characteristic pustules or agglomerations. For the inclusions to form there must be slow migration of material through the paint film, leading to the formation of coagulated masses of lead soaps. This migration, and the subsequent growth of the inclusion, has in many cases led to distortion of the surrounding paint layers. It is not clear how quickly the inclusions form; it might be expected that lead soaps will be most mobile when the paint film is young. Test samples of red lead in linseed oil painted out about ten years ago show soap formation, but these films have not yet formed inclusions. The process of pustule formation (as opposed to lead carboxylate formation) is therefore probably quite slow.[49]

Free fatty acids or metal carboxylates which have migrated through the paint have been observed on the surface of paintings, in the form of a bloom or efflorescence.[50] While this is clear evidence of their mobility, what is not so obvious is what drives the migration and aggregation. Williams suggests that increased cross-linking and changes in polarity during ageing can lead to incompatibilities between components that cause separation and blooming.[51] Van den Berg expands on this idea in his discussion of the migration of fatty acids (and the arguments are equally applicable to metal carboxylates), suggesting that a phase separation occurs when the less polar saturated fatty acids are driven out of the polar oil network.[52] Thus, the initially uniform distribution of lead soaps throughout a film may result in a stable system, but as the film ages, this arrangement ceases to be favourable and migration and aggregation occur.

There is also evidence that there may be a 'concentration factor' involved, with migration only occurring once fatty acids or metal carboxylates have reached a critical level.[53] The amount of free fatty acid present in a drying oil is dependent on the type of oil and how it has been prepared, and it seems likely that this will have an influence on the degree to which inclusions are formed.[54] An alternative to the phase separation theory has been suggested by Ordonez and Twilley,[55] based on the work of Whitmore et al.[56] They suggest two factors are important: (i) oil paintings may be subject to conditions of temperature and humidity such that the polymerised oil matrix is above its glass transition temperature but the free fatty acids are below their melting point; and (ii) the crystal morphology of free fatty acids may be such that when molecules assume a favourable orientation, they 'freeze' in position.[57] Although the soaps in the inclusions do not appear to be crystalline (indeed it is difficult to prepare crystalline samples of lead palmitate or stearate), there is likely to be a high degree of intermolecular order within these regions,[58] perhaps contributing to the driving force that separates the metal soaps from the more amorphous oil film matrix.

The main components of the inclusions have been shown to be the metal soaps of palmitic and stearic acids (both saturated monocarboxylic acids).[59] Lead soaps of other fatty acids that are found in drying oils, such as dicarboxylic acids and unsaturated monocarboxylic acids, are known,[60] but these species have not been found in inclusions or blooms;[61] it appears, therefore, that only the palmitate and stearate migrate through the film. In the inclusions they have coagulated together and concentrated, perhaps because they are the most hydrophobic of the soaps, and the agglomerations have grown to the point where they have displaced the surrounding matrix, including the less hydrophobic lead soaps.

The absence of unsaturated fatty acid soaps (such as oleate and linoleate) in inclusions may be because they are more likely to undergo cross-linking reactions or decomposition,[62] or because of the poor (solid-solution) 'miscibility' of the saturated and unsaturated fatty acids reported by Ordonez and Twilley.[63] Similarly, the fact that lead soaps of dicarboxylic acids (such as lead azelate) have not been detected in inclusions may be because the dicarboxylic acids (and by analogy their lead soaps) have very different chemical and physical properties to the saturated monocarboxylic acids (such as palmitic and stearic acids) or their lead soaps. The dicarboxylic species are much more polar (having much shorter hydrocarbon chains and difunctionality), so their incorporation into the inclusions will not be favoured. The shorter hydrocarbon chain and difunctionality also means that the dicarboxylates will not be readily compatible with the ordered lamellar structure that is likely to exist in regions containing long chain monocarboxylate soaps.[64] Further, the dicarboxylics have higher melting points and two carboxylic acid groups (increasing the chance of reaction), making them much less mobile than the monocarboxylics.[65]

If this model of inclusion formation is correct, it may help to explain the 'low azelate effect' mentioned earlier.[66] From the results presented in Table 1, it can be seen that where inclusions have been separated out from the bulk, low azelate to palmitate ratios are detected, but that for other whole samples, only slightly lowered, or sometimes normal, ratios are obtained. It seems likely that in the paint film as a whole, azelaic acid (and lead azelate) form normally as the oil dries, but that areas in the film containing pustules will become enriched in palmitate and stearate because of the migration of these species into the inclusions from elsewhere in the film. As a result, if a sample contains a high proportion of pustules, then enhanced palmitate and stearate levels are detected and hence (apparently) lowered azelate to palmitate ratios. If a larger sample is examined, or one in which inclusions are only a small part, then normal ratios will be seen for the sample overall.

Conclusions

Translucent lead soap inclusions are commonplace in oil films containing red lead or lead-tin yellow. They comprise lead fatty acid soaps (of saturated fatty acids) and lead carbonate, and form as a result of reaction of the pigment with the oil binding medium. Although the paintings in this study are from a broad range of geographical locations and dates, demonstrating the widespread nature of this phenomenon, the results of analysis were extremely consistent, the main difference being the size, rather than the composition, of the inclusions. Some variation in the opacity of the inclusions can be accounted for by differences in the proportion of lead carbonate to lead soap in the inclusions. Inclusions have most commonly been noted in lead-tin yellow paint layers as this pigment is often used on its own.

In paintings dating from before the nineteenth century, the lead soap inclusions are not likely to be a deliberate addition to the original paint, as they serve no obvious purpose; they would have siccative properties but the lead pigments with which they are found are themselves good driers. The coarse and lumpy texture of the paint where inclusions are large is unlikely to be a deliberate effect intended by the artist, as has sometimes been thought. Instead, the inclusions will have formed over a period of time, after the painting was completed, by migration and agglomeration of the lead fatty acid soaps. Although the rate of formation of the inclusions is still unclear, the changes in the density and polarity of the paint film and the build-up of fatty acid soaps as it ages may be important factors.

The fatty acid ratios obtained from GC–MS analysis are vital to the identification of paint binding media. The level of azelaic acid present is particularly useful in distinguishing drying oils from materials containing non-drying fats, such as egg tempera. The presence of inclusions within a paint layer has been shown to affect the fatty acid ratios. Low levels of azelaic acid have regularly been found, which could lead (and have led in the past) to the erroneous conclusion that the binding medium of the paint is egg tempera, or that a mixed medium or emulsion has been used. FTIR microscopy has, however, confirmed that none of the samples examined in this study contain protein. Thus, inclusion formation has consequences for the interpretation of the results of binding medium analysis, particularly if GC–MS is the only analytical technique employed.

The misidentification of the binder has a number of implications. For example, the widely held belief that Early Netherlandish painters used emulsions for lead-tin yellow highlights needs to be reassessed in the light of the findings in this paper. Inclusions may also pose a problem during cleaning of paintings, as the rather soft waxy lead soaps are vulnerable to mechanical damage. This is evident in Moretto's *Madonna and Child with Saints* (NG 1165) where the tops of the pustules have been flattened (PLATE 3b). However, lead soaps do not seem to be particularly soluble in commonly used cleaning agents.[67] The rough, gritty surface created by the inclusions can also cause problems during varnishing. Dirt sometimes becomes trapped in the soft lead soaps when they are exposed at the paint surface, which can be visually disturbing in light areas of paint; the white spots created by exposed pustules in dark paint are similarly very noticeable. Thus, a better understanding of the origin and chemistry of lead soap inclusions is important for the interpretation and conservation of the wide range of paintings that demonstrate this phenomenon.

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terisation of lead azelate. Thanks are also due to Janet Ambers of the British Museum Research Laboratory for assisting us with Raman microscopy.

Notes and references

1 H. Howard, *Pigments of English Medieval Wall Painting*, London 2003; P.C. van Geersdaele and L.J. Goldsworthy, 'The Restoration of Wallpainting Fragments from St. Stephen's Chapel, Westminster', *The Conservator*, 2, 1978, pp. 9–12.

2 A.J. Eikhoff, 'Pigmentation of Coatings', *Pigment Handbook,* Vol. II: *Applications and Markets*, ed. T.C. Patton, New York 1973, pp. 49–55; R.J. Gettens and G.L. Stout, *Painting Materials: A Short Encyclopedia*, New York 1942 (reprinted New York 1966), p. 153; E. West Fitzhugh, 'Red Lead and Minium', *Artists' Pigments: a Handbook of their History and Characteristics*, Vol. I, ed. R.L. Feller, New York 1986, pp. 109–39.

3 D. Saunders, M. Spring and C. Higgitt, 'Colour change in red lead-containing paint films', *ICOM–CC 13th Triennial Meeting*, Rio de Janeiro 2002, pp. 455–63.

4 L. Kockaert, 'Note sur les émulsions des Primitifs flamands', *Institut Royal du Patrimoine Artistique Bulletin*, XIV, 1973/4, pp. 133–9.

5 See Kockaert 1973/4, cited in note 4; J.R.J. van Asperen de Boer, M. Faries and J.P. Filedt Kok, 'Painting technique and workshop practice in Northern Netherlandish Art of the sixteenth century', in *Kunst voor de beeldenstorm*, Amsterdam 1986, p. 109; van Geersdaele and Goldsworthy 1978, cited in note 1; L.E. Plahter and U.S. Plahter, '*The young Christ among the doctors* by Teodoer van Baburen: Technique and condition of a Dutch seventeenth century painting on canvas', originally published in *Acta ad archaeologiam et artium historiam pertinentia*, Vol. III, 1983 and reprinted in *Conservare Necesse Est*, *for Leif Einar Plahter on his 70th Birthday*, IIC Nordic Group, Oslo 1999, pp. 42–65.

6 U. Plahter, 'Baburen re-examined'*, Conservare Necesse Est,* cited in note 5, pp. 66–7.

7 Some of the preliminary work described in this article was presented as a paper (C. Higgitt, M. Spring and D. Saunders, 'Pigment-medium interactions in oil paint films containing red lead or lead-tin yellow') at the joint meeting of ICOM–CC Working Groups Paintings 1 and 2 and The Paintings Section, UKIC, *Deterioration of Artists' Paints: Effects and Analysis*, held at the British Museum, 10–11 September 2001 (pp. 21–6 of the extended abstracts). Other studies are listed below: K. Brunnenkant, 'Falscher Glanz? Technologische Untersuchung des "W.Kalf.1643" signierten Prunkstillebens im Wallraf-Richartz-Museum in Köln und Vergleich mit Werken aus der Pariser Periode Willem Kalfs (ca. 1619–1693)', *Zeitschrift für Kunsttechnologie und Konservierung*, 13, 1999, pp. 245–84; *Still Lifes: Techniques and Style, The Examination of Paintings from the Rijksmuseum*, ed. A. Wallert, Amsterdam 1999, p. 112; J.J. Boon, J. van der Weerd, K. Keune, P. Noble and J. Wadum, 'Mechanical and chemical changes in Old Master paintings: dissolution, metal soap formation and remineralization processes in lead pigmented ground/intermediate paint layers of 17th century paintings', *ICOM–CC 13th Triennial Meeting*, Rio de Janeiro 2002, pp. 401–6; J. van der Weerd, J.J. Boon, M. Geldof, R.M.A. Heeren and P. Noble, 'Chemical Changes in Old Master Paintings: Dissolution, Metal Soap Formation and Remineralisation Processes in Lead Pigmented Paint Layers of 17th Century Paintings', *Zeitschrift für Kunsttechnologie und Konservierung*, 16, 2002, pp. 36–51.

8 Plahter 1999, cited in note 6.

9 R. White, 'Van Dyck's Paint Medium', *National Gallery Technical Bulletin*, 20, 1999, p. 88.

10 N. Middelkoop, P. Noble, J. Wadum and B. Broos, *Rembrandt Under the Scalpel: The Anatomy Lesson of Dr Nicolaes Tulp Dissected*, exh. cat., Mauritshuis, The Hague and Amsterdam 1998, pp. 57–8; R.M.A. Heeren, J.J. Boon, P. Noble and J. Wadum, 'Integrating imaging FTIR and secondary ion mass spectrometry for the analysis of embedded paint cross-sections', *ICOM–CC 12th Triennial Meeting*, Lyon 1999, pp. 228–33; P. Noble, J. Wadum, K. Groen, R. Heeren and K.J. van den Berg, 'Aspects of 17th century binding medium: inclusions in Rembrandt's *Anatomy lesson of Dr Nicolaes Tulp', Art et Chemie, la couleur: Actes du Congrès*, Paris 2000, pp. 126–9.

11 Howard 2003, cited in note 1, and S. Bucklow, 'Technique', *The Thornham Parva Retable: Technique, Conservation and Context*, ed. A. Massing, London 2003, in press.

12 M.A. Mesubi, 'An Infrared Study of Zinc, Cadmium and Lead Salts of some Fatty Acids', *Journal of Molecular Structure*, 81, 1982, pp. 61–71; L.J. Bellamy, *The Infrared Spectra of Complex Molecules,* Vol. 1, 2nd edn, Cambridge 1975; N.P.G. Roeges, *A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures*, Chichester 1994; R. Matura, 'Divalent metal salts of long chain fatty acids', *Journal of the Chemical Society of Japan*, 86, 1965, pp. 560–72. It should be noted that in addition to the simple metal(II) (M^{II}) soap stoichiometry, M^{II}(monocarboxylate)$_2$ or M^{II}(dicarboxylate), other stoichiometries are possible, for example acidic and basic soaps. See M.S. Akanni, E.K. Okoh, H.D. Burrows and H.A. Ellis, 'The thermal behaviour of divalent and higher valent metal soaps: a review', *Thermochimica Acta*, 208, 1992, pp. 1–41; M.L. Lynch, F. Wireko, M. Tarek and M. Klein, 'Intermolecular Interactions and the Structure of Fatty Acid-Soap Crystals', *Journal of Physical Chemistry B*, 105, 2001, pp. 552–61; C.T. Morley-Smith, 'Zinc Oxide – A Reactive Pigment', *Journal of the Oil and Colour Chemists' Association*, 41, 1958, pp. 85–97; A. E. Jacobsen and W. H. Gardner, 'Zinc soaps in paints: zinc oleates', *Industrial and Engineering Chemistry*, 33, 1941, pp. 1254–6. Normal lead stearate ($Pb(C_{17}H_{35}COO)_2$, CAS No. 1072-35-1) and dibasic lead stearate ($2PbO{\cdot}Pb(C_{17}H_{35}COO)_2$, CAS No. 12578-12-0) are available as PVC additives (infrared spectra available via FDM FTIR Spectra Database of Surfactants, Fiveash Data Management Inc., www.fdmspectra.com), and the basic and tribasic lead stearates are also known.

13 J.S. Mills and R. White, *The Organic Chemistry of Museum Objects*, 2nd edn, London 1994, pp. 33 and 171.

14 The C–H stretches are strong, sharp and well resolved in infrared spectra of the inclusions compared to those for the surrounding matrix. This suggests that the number of separate organic components present in the inclusion is more limited than in the matrix and that these components are not changing with time.

15 Similar clearly resolved lead carboxylate infrared spectra were also obtained from inclusions within a lead-tin yellow highlight and a red lead-containing underpaint in Dujardin's *Portrait of a Young Man (Self Portrait?)*, NG 1680 (see Table 1).

16 Raman spectroscopy was also used to investigate the components in the inclusions. Again, each of the three lead soaps could be distinguished in the pure form (with the lead palmitate and stearate being practically identical). However, in samples from paintings the soap bands were completely masked by the lead pigments present in the sample and/or fluorescence. Similar results were reported by L. Robinet and M.-C. Corbeil, 'The characterization of Metal Soaps', *Studies in Conservation*, 48, 2003, pp. 23–40.

17 E. Childers and G.W. Struthers, 'IR Evaluation of Sodium Salts of Organic Acids', *Analytical Chemistry*, 27, 1955, pp. 737–41. The authors note that, in some cases, the co-precipitated salts of a mix of organic acids will not give exactly the same infrared spectrum as is obtained by mixing the pure salts. They relate this observation to the crystal structure of the co-precipitated material.

18 The infrared spectrum obtained by the combination of the spectra of standards of lead palmitate and stearate gives a very close match to the spectrum for the inclusions in the Hobbema, even down to the fine structure in the 1350–1180 cm^{-1} region.

19 R. White and J. Pilc, 'Analyses of Paint Media', *National Gallery Technical Bulletin*, 17, 1996, p. 95.

20 Mills and White 1994, cited in note 13.

21 Van Geersdaele and Goldsworthy 1978, cited in note 1.

22 J. Pilc and R. White, 'The Application of FTIR-Microscopy to the Analysis of Paint Binders in Easel Paintings', *National Gallery Technical Bulletin*, 16, 1995, pp. 73–84; R.J. Meilunas, J.G. Bentsen and A. Steinberg, 'Analysis of Aged Paint Binders by FTIR Spectroscopy', *Studies in Conservation*, 35, 1990, pp. 33–51.

23 Kockaert 1973/4, cited in note 4. False positive results have been obtained when using amido black as a stain, with lead white being stained erroneously, J. Kirby, National Gallery, personal communication.

24 Plahter and Plahter 1983 (1999), cited in note 5.

25 Eikhoff 1973 and West Fitzhugh 1986, both cited in note 2; E.J. Dunn, Jr, 'Red Lead', *Pigment Handbook,* Vol. I: *Properties and Economics*, ed. T.C. Patton, New York 1973, pp. 837–42; J.E.O. Mayne, 'Pigment Electrochemistry', *Pigment Handbook,* Vol. III: *Characterisation and Physical Relationships*, ed. T. C. Patton, New York 1973, pp. 457–64; J.E.O. Mayne, 'The protective Action of Lead Compounds', *Journal of the Society of the Chemical Industry*, 65, 1946, pp. 196–204; J.E.O. Mayne, 'The Pigment/Vehicle Relationship in Anti-corrosive Paints', *Journal of the Oil and Colour Chemists' Association*, 34, 1951, pp. 473–9.

26 A.F. Wells, *Structural Inorganic Chemistry*, 5th edn, Oxford 1984, p. 559; R.J.H. Clark, L. Cridland, B.M. Kariuki, K.D.M. Harris and R. Withnall, 'Synthesis, Structural Characterisation and Raman Spectroscopy of the Inorganic Pigments Lead Tin Yellow Types I and II and Lead Antimonate Yellow: Their Identification on Medieval Paintings and Manuscripts', *Journal of the Chemical Society, Dalton Transactions*, 1995, pp. 2577–82.

27 E.J. Dunn, Jr, 'Lead Pigments' in *Treatise on Coatings,* Vol. 3: *Pigments, pt. 1*, eds R.R. Myers and J.S. Long, New York 1975, pp. 403–4. In addition, Dunn in 'White Hiding Lead Pigments', in *Pigment Handbook,* Vol. I, cited in note 25, p. 66, notes that 'white leads are chemically active pigments. They react with both the free acidic portions of vehicles and with the breakdown acids that develop from paint vehicles as paint films age. The reaction products, … which are called lead soaps, reinforce the paint film. Fortunately these white lead reaction products are formed at a favorable (slow) rate that imparts the right type of plasticity to the paint film for good stabilisation.' See also L.A. O'Neill and R.A. Brett, 'Chemical reactions in paint films', *Journal of the Oil and Colour Chemists' Association*, 52, 1969, pp. 1054–74. The authors demonstrated that for pigments in linseed oil, appreciable reaction occurred with basic oxide pigments (red lead and zinc oxide), rather less with carbonates (lead white) and little or none with inert oxides.

28 Mayne 1946, cited in note 25. Lead, litharge (PbO) and red lead were found to reduce corrosion, while basic lead carbonate and lead chromate did not. Mayne links these findings to the relative amounts of lead(II) ions produced in solution.

29 Studies carried out at the National Gallery have shown that in ten-year-old test films containing lead white in oil, there is some lead carboxylate formation, but that these have a uniform distribution and are not present as inclusions. Pure lead white paint films from paintings give the same result.

30 It has been proposed in the literature (Boon et al. 2002, cited in note 7) that lead fatty acid soap inclusions form from the reaction of an unstable form of lead white with an oil medium. In all of the examples, other pigments are also present which could be the source of the lead soaps and, for the reasons discussed later in this text, seem more likely. Indeed, in more recent papers in the literature, this possibility has been acknowledged, see van der Weerd et al. 2002, cited in note 7.

31 L. Carlyle, 'Paint Driers Discussed in 19th-Century British Oil Painting Manuals', *Journal of the American Institute for Conservation*, 38, 1999, pp. 69–82; L. Carlyle, *The Artist's Assistant*, London 2001, pp. 41–54.

32 Examination by J. Zucker in 'From the Ground Up: The Ground in 19th-Century American Pictures', *Journal of the American Institute for Conservation*, 38, 1999, pp. 3–20, and by J.D.J. van den Berg in *Analytical Chemical Studies on Traditional Linseed Oil Paints*', PhD Thesis, University of Amsterdam, 2002, Chapter 7, of a primed canvas and an unfinished canvas belonging to the American painter Frederic Edwin Church revealed that each showed bloom formation, ground staining and protrusions. Zucker's and van den Berg's studies suggest that these three types of paint defect may be linked, and detailed analysis by van den Berg has revealed that the bloom and the protrusions contain primarily lead stearate and lead palmitate. In 1885, Church linked the ground staining that had appeared on his canvases to the inclusion of sugar of lead (lead acetate) in the ground preparation used by the canvas-maker Winsor & Newton (Zucker, pp. 11 and 13). A number of nineteenth-century writers warn of the problems of the use of lead acetate as a drier. For example, G. Field in *Chromatography; or A treatise on colours and pigments, and their powers in painting*, London 1835, p. 56 states: 'The inexperienced ought here to be guarded also from the highly improper practice of some artists, who strew their pictures while wet with the acetate of lead, … which, though it may promote present drying, will ultimately effloresce on the surface of the work, and throw off the colour in sandy spots'. A.H. Church in *The Chemistry of Paints and Painting*, London 1890, p. 94, again warns: 'I have seen one of the results of this commingling of sugar of lead with the medium or the paint in the production of sugar of lead with the medium or the paint in 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'. He continues his discussion, suggesting that the efflorescence attracts 'carbonic acid from the air and becomes lead carbonate' which he suggests could then darken to lead sulphide. These quotes are also discussed in Carlyle 1999 (p. 75) and Carlyle 2001 (p. 45), both cited in note 31.

33 J. Koller and A. Burmester, 'Blanching of unvarnished modern paintings: a case study on a painting by Serge Poliakoff', in *Cleaning, Retouching and Coatings: Technology and Practice for Easel Paintings and Polychrome Sculpture*, eds J.S. Mills and P. Smith, London 1990, pp. 138–43. In addition, N. Heaton states in his *Outlines of Paint Technology*, London 1948, p. 73 that '…zinc oxide reacts with oil in an even more pronounced manner than white lead, owing to its basic character. The reaction with oil is somewhat different from that of lead, the acceleration of the drying not being so pronounced, and the film formed on drying being hardened in a pronounced manner. Zinc oxide paints, therefore, tend to dry hard and non-elastic, and are inclined to become brittle and crack on exposure to the weather'. See also O'Neill and Brett 1969, cited in note 27, and Morley-Smith 1958, cited in note 12. For examples where zinc soaps have been detected in paintings see M.-C. Corbeil, P.J. Sirois and E.A. Moffat, 'The use of a white pigment patented by Freeman by Tom Thomson and the Group of Seven', *ICOM–CC 12th Triennial Meeting* , Lyon 1999, pp. 363–8 (where zinc soaps were detected by FTIR and result from the reaction of the zinc white in the lead sulphate/zinc white mix), and J. van der Weerd, *Microspectroscopic Analysis of Traditional Oil Paint*, PhD Thesis, University of Amsterdam, 2002, Chapter 8.

34 Similar results are reported (based on laser microspectral analysis) for a lead-tin yellow highlight from Belshazzar's cloak in Rembrandt's *Belshazzar's Feast* (NG 6350), as illustrated in H. Kühn, 'Lead-Tin Yellow', *Artists' Pigments: a Handbook of their History and Characteristics*, Vol. II, ed. A. Roy, New York 1993, p. 91.

35 For a discussion of tin white see R.D. Harley, *Artists' Pigments c. 1600–1835*, 2nd edn, London 1982, pp. 172–3. Tin oxide has also been reported in a seventeenth-century painting by Jan Steen, but since it was found in a lead-tin-yellow-containing paint it is possible that it is there as a deterioration product. See M. Palmer and E.M. Gifford, 'Jan Steen's Painting Practice: *The Dancing Couple* in the Context of the Artist's Career', *Studies in the History of Art 57, Conservation research 1996/1997*, Washington 1997, pp. 127–56, especially p. 151.

36 A. Burmester and C. Krekel, '"Azurri oltramarini, lacche e altri colori fini": The Quest for the Lost Colours', in C. Syre, *Tintoretto, The Gonzaga Cycle*, Munich 2000, pp. 213–26. The identification of tin oxide is listed in Table 3, p. 206, and the interpretation is discussed in note 31, p. 210.

37 S. Giovannoni, M. Matteini and A. Moles, 'Studies and developments concerning the problem of altered lead pigments in wall paintings', *Studies in Conservation*, 35, 1990, pp. 21–5. N.N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Oxford 1984, Chap. 10. The authors observe that 'Because of the instability of Pb(IV), PbO_2 tends to give salts of Pb(II) with liberation of O_2 when treated with acids'. Further, in her article on red lead, West Fitzhugh 1986, cited in note 2, notes that PbO_2 is an oxidising agent and that it decomposes slowly due to the action of light or gentle heat.

38 Experiments conducted at the National Gallery have shown that, in the presence of carbon dioxide and moisture, PbO_2 in oil converts to basic lead carbonate (reported in Saunders et al. 2002, cited in note 3). It therefore seems likely that the Pb(IV)-containing residue from red lead (after lead(II) soaps have formed) reacts with carbon dioxide, moisture and/or other components of, or degradation products in, the oil film to form lead(II) species.

39 Saunders et al., cited in note 3. That the conversion of red lead to basic lead carbonate can also occur in media other than oil indicates that a direct reaction is possible (that is, lead carboxylate formation need not mediate the reaction). In the accelerated ageing studies on oil-containing films, it was not possible to recreate the pustule morphology described here. Lead fatty acid soaps were detected by FTIR (in addition to basic lead carbonate), but these appeared to be dispersed throughout the paint film and there was no evidence for the formation of large lead fatty acid soap inclusions. On test films painted out about ten years ago, no basic lead carbonate was detected for the control samples (kept in the dark). Instead, very fine whitish, opaque 'blooms' or 'patches' could just be made out on the surface, using a microscope, and lead fatty acid soaps were detected by FTIR. Again, no evidence of pustule formation was observed. Thus it seems likely that the development of lead fatty acid soap inclusions is a slower process, and only occurs if red lead is not more rapidly converted to lead carbonate by the action of high levels of moisture and light.

40 Eikhoff 1973 and West Fitzhugh 1986, both cited in note 2.

41 R.M. Garrels and C.L. Christ, *Solutions, Minerals and Equilibria*, London 1965, Chap. 7; Greenwood and Earnshaw 1984, cited in note 37. As discussed in note 30, lead white has been proposed as the source for lead fatty acid soap inclusions. In these studies, complex local chemical environments have been proposed to explain the authors'

observation of the formation of lead carboxylates and the 'remineralisation' of lead white, basic lead chloride and minium from a lead white film. Lead white is proposed to lose carbon dioxide and water to leave lead oxides and hydroxides that react with the oil medium components (reported by K. Keune, P. Noble and J. Boon in the paper 'Chemical changes in lead-pigmented oil paints: on the early stage of formation of the protrusions' presented at *Art 2002*, 7th International Conference on Non-destructive Testing and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage, Antwerp 2002). Keune suggested in her presentation that a highly acidic environment would be required to decompose lead white (this point is not very clearly stated in the preprints). The pH is then proposed to swing to highly basic conditions locally (pH > 10, van der Weerd et al. 2002, cited in note 7) in order to explain the precipitation of minium and the re-precipitation of lead white. It is suggested that it is the dissolution of the lead white and the release of carbonate and hydroxide moieties that lead to the high pH environment. The alternative model proposed in this article avoids the need for extreme pH conditions in the paint film.

42 If basic soaps are formed, it is possible that the 'PbO' associated with the soap forms the lead carbonate, see note 12.

43 See note 38.

44 Carboxylic acids have been shown to undergo facile thermal or photochemical oxidative decarboxylation in the presence of oxidising metal ions such as Pb(IV). See R.A. Sheldon and J.K. Kochi, 'Oxidative Decarboxylation of Acids by Lead Tetraacetate', in *Organic Reactions*, Vol. 19, eds R. Bittman, W.G. Dauben, J. Fried, A.S. Kende, J.A. Marshall, B.C. McKusick, J. Meinwald and B.M. Trost, New York 1972, pp. 279–421.

45 In accelerated ageing studies it has not proved possible to form lead carbonate from lead soaps, but the reaction is likely to be very slow and may be highly dependent on the pH (i.e. in a slightly acidic aged oil medium) and whether the environment is hydrophobic or hydrophilic. In a related reaction, lead acetate is readily converted to lead carbonate or basic lead carbonate, Greenwood and Earnshaw 1984, cited in note 37.

46 In two of the paintings in this study, Veronese's *Adoration of the Kings* (NG 268), 1573, and *Cleopatra* (NG 5762) by an anonymous French painter of the sixteenth century, a small amount of chloride was detected by EDX analysis in the inclusions. Noble et al. 2000, cited in note 10, also found some chloride in inclusions in Rembrandt's *The Anatomy Lesson of Dr Nicolaes Tulp*, which they were able to establish was present as lead hydroxychloride. The most likely source of chloride is from the environment – it is often present in dirt.

47 J. Cartwright, J. Manuel Garcia-Ruiz and A.I Villacampa, 'Pattern formation in crystal growth: Liesegang rings', *Computer Physics Communications,* 121, 1999, pp. 411–13.

48 This seems to be the case in lead white films examined. See also note 29.

49 See note 39.

50 E. Ordonez and J. Twilley, 'Clarifying the Haze: Efflorescence on Works of Art', *Analytical Chemistry*, 69, 1997, pp. 416A–22A; S.R. Williams, 'Blooms, Blushes, Transferred Images and Moldy Surfaces: What are these Disfiguring Accretions on Art Works?', *Proceedings of the 14th annual IIC–CG conference*, Toronto 1989, pp. 65–84; B. Singer, J. Devenport and D. Wise, 'Examination of a blooming problem in a collection of unvarnished oil paintings', *The Conservator*, 19, 1995, pp. 3–9; van den Berg 2002, cited in note 32; Koller and Burmester 1990, cited in note 33; A. Burnstock, M. Caldwell and M. Odlyha, 'A Technical Examination of Surface Deterioration of Stanley Spencer's Paintings at Sandham Memorial Chapel', *ICOM–CC 10th Triennial Meeting*, Washington 1993, pp. 231–8. The ratio of palmitic to stearic acids in the inclusions (and blooms) is generally found to give a good match to that in the paint, indicating that the oil is the source of the palmitate and stearate (Ordonez and Twilley, Koller and Burmester, Singer et al., van den Berg cited above).

51 Williams 1989, cited in note 50, states that 'increases in cross-link density (causing film shrinkage and syneresis) and changes in polarity of oxidized components (causing changes in solubility parameter) can create incompatibilities between components that can lead to separation and blooming, especially of scission products produced by oxidative degradation'. See also Ordonez and Twilley 1997, cited in note 50; G. Thomson, 'Some Picture Varnishes', *Studies in Conservation*, 3, 1957, p. 70.

52 Van den Berg 2002, cited in note 32, comments that 'Fatty acids that are not chemically or physically trapped within the paint might be driven out because of difference(s) in polarity between the polar networks and the apolar saturated FAs (fatty acids), in other words, a 'phase' separation occurs. The fact that, as far as (is) known, no diacids have been observed in the bloom supports this theory.' An alternative view is presented by Koller and Burmester 1990, cited in note 33. They argue that the volume of the paint medium around metal soap agglomerations is reduced by losses during drying and ageing. Therefore, as the paint medium contracts on ageing, the agglomerations start to project through the paint surface.

53 The fact that we have not observed inclusions in lead white films may reflect the lower reactivity of lead white (and hence lower soap concentrations) compared to red lead. Dunn 1973 and Dunn 1975, both cited in note 27.

54 Carlyle 1999 (p. 73), cited in note 31, suggests that some of the problems associated with the use of excess driers in nineteenth-century paint formulations might be linked to the formation of excessively high levels of lead soaps. Koller and Burmester 1990, cited in note 33, suggest that the use of stand oil (with its higher levels of free fatty acids than linseed oil) was important to the formation of bloom. Van der Weerd 2002, cited in note 33, suggests that fatty acids would not be immediately available in fresh paint, and that time would be needed for glyceride hydrolysis, a process that could take several decades (see also J.D.J. van den Berg, K.J. van den Berg and J.J. Boon, 'Determination of the degree of hydrolysis of oil paint samples using a two-step derivatisation method and on-column GC/MS', *Progress in Organic Coatings*, 41, 2001, pp. 143–55). But this hypothesis assumes that the presence of free fatty acids is required prior to carboxylate formation (see notes 29 and 39).

55 Ordonez and Twilley 1997, cited in note 50.

56 P.M. Whitmore, V.G. Colaluca and E. Farrell, 'A note on the origin of turbidity in films of an artist's acrylic paint medium', *Studies in Conservation*, 41, 1996, pp. 250–5.

57 Under such conditions, fatty acids migrate until they encounter a nucleation site where they orient in their preferred position to 'grow'. The polymerised oil matrix is mobile enough to accommodate the growth. See Ordonez and Twilley 1997, cited in note 50, p. 421A.

58 The low symmetry and difficulties in the isolation of pure single crystals of metal soaps makes complete structure analysis difficult, Akanni et al. 1992, cited in note 12. However, these materials have been shown to adopt ordered lamellar structures. See J.-M. Rueff, N. Masiocchi, P. Rabu, A. Sironi and A. Skoulios, 'Structure and Magnetism of a Polycrystalline Transition Metal Soap – $Co^{II}[OOC(CH_2)_{10}COO](H_2O)_2$', *European Journal of Inorganic Chemistry*, 2001, pp. 2843–8; J.-M. Rueff, N. Masiocchi, P. Rabu, A. Sironi and A. Skoulios, 'Synthesis, Structure and Magnetism of Homologous Series of Polycrystalline Cobalt Alkane Mono- and Dicarboxylate Soaps', *Chemistry – A European Journal*, 8, 2002, pp. 1813–20. Lead palmitate and stearate contain both polar and non-polar groups within the same molecule and are therefore able to show orientation phenomena, surfactant-like behaviour and form sols, gels and pastes. See R.C. Mehrotra and R. Bohra, *Metal Carboxylates*, London 1983, pp. 151–6. See also note 12 in the Appendix. Mesubi 1982, cited in note 12, in his study of the effect of temperature on the infrared spectra of zinc, cadmium and lead fatty acid soaps, notes that the doublet around 720 cm^{-1} (CH_2 rocking mode), seen at room temperature, indicates that the hydrocarbon chains of the soaps are in a crystalline state under ambient conditions. As the temperature is raised towards the melting point, the doublet becomes broad and the fine structure in the 1350–1180 cm^{-1} regions disappears, indicating that the hydrocarbon chains of soaps can approach a 'liquid-like' state while the 'Pb–O' part of the structure remains unaltered (asymmetric and symmetric COO stretches unaltered).

59 Noble et al. 2000 and Heeren et al. 1999, both cited in note 10; O'Neill and Brett 1969, cited in note 27; van den Berg 2002, cited in note 32; van der Weerd 2002, cited in note 33.

60 Lead azelate has been prepared during the course of this study. W. Brzyska and H. Warda, 'Preparatyka I Własciwosci Ałkanodikarboksyłanów Ołowiu (II)', *Rudy I Metale Niezelazne*, 28, 1983, pp. 204–8; A.J. Appleby and J.E.O. Mayne, 'Corrosion inhibition by the salts of the long chain fatty acids', *Journal of the Oil and Colour Chemists' Association*, 50, 1967, pp. 897–910. Metal oleates and linoleates prepared by M.-C. Corbeil and L. Robinet, 'X-ray powder diffraction data for selected metal soaps', *Powder Diffraction*, 17, 2002, pp. 52–60.

61 Koller and Burmester 1990, cited in note 33, report the presence of metal soaps of azelaic, palmitic, oleic, stearic and isomerised linoleic (from the use of stand oil) acids in paint films.

62 Mayne 1973, cited in note 25, reports the results of a study of the

degradation of the lead soaps of individual fatty acids. The saturated acid soaps did not degrade or render water non-corrosive. Oleic, linoleic and linolenic soaps degraded to give inhibitive materials – extracts of the soaps of unsaturated acids contained water-soluble peroxides. However, the major degradation product was lead azelate. It should be noted that lead azelate was not detected in inclusions in the present study.

63 Ordonez and Twilley 1997, cited in note 50, p. 417A.

64 See note 58.

65 The lead palmitate prepared for this study had a melting point of ~112°C, in good agreement with the literature (112.3°C, *CRC Handbook of Chemistry and Physics,* 68th edn, ed. R.C. Weast, Boca Raton 1987, p. B100). The sample of lead azelate started to turn grey at around 239°C, and had become very dark by 250°C when heating was stopped. The sample had not melted by this stage.

66 This phenomenon is not fully understood and other explanations may be possible: (i) decomposition of lead azelate may occur in the inclusions (possibly by decarboxylation, see note 44); (ii) azelaic acid may not be effectively released from lead soaps by TMTFTH in GC analysis; (iii) lead pigments may be less reactive towards azelaic acid than palmitic and stearic acids; (iv) the drying process and oxidative degradation to form azelaic acid may be affected by the presence of red lead, lead-tin yellow or lead soaps.

67 At room temperature, the lead carboxylates prepared in this study were extremely insoluble in water and in all common organic solvents. Contrary to the findings of B.K. Chatterjee and S.R. Palit, 'Solubilising effect of some basic organic compounds on lead and zinc soaps', *Journal of the Indian Chemical Society*, 31, 1954, pp. 421–5, there was no evidence for solubility in glycols or amines (glycol and triethanolamine were tested). It is suggested by van den Berg 2002, cited in note 32 (p. 48), that metal carboxylates will be vulnerable to citrates and other chelating cleaning agents and he cites studies where surface damage has occurred due, most probably, to loss of metal ions. However, triammonium citrate did not appear to have any effect on the soaps when tested in the laboratory, but further study should be undertaken.

TABLE 1 Summary of results of analysis

Artist, painting title and date	Description of the paint layers containing inclusions	Content of inclusion	GC–MS results; oil type, azelate/palmitate ratio (A/P)
Nathaniel Bacon, *Cookmaid with Still Life of Vegetable and Fruit*, 1620–5, Tate Britain.	Pale yellow highlight on the gourd; lead-tin yellow.[a]	Lead soaps and basic lead carbonate,[b] more carbonate than soaps.[c]	Partially heat-bodied linseed oil, A/P 1.4.
Bartholomeus van Bassen, *An Imaginary Church*, 1627, Brighton Museum and Art Gallery.	Red ground layer; red earth and red lead. Second brownish-grey ground layer; lead white, black, brown, red lead.	Lead soaps and basic lead carbonate,[b] in approximately equal amounts.[c]	Linseed oil, A/P 0.24.
Giovanni Bellini, attributed to, *Adoration of the Kings* (NG 3098), *c.*1490.	Pale yellow robe of the figure between the two horses on the right; lead-tin yellow.[a]	Lead soaps and lead carbonate,[b] more soaps than carbonate.[c]	Partially heat-bodied drying oil, A/P > 1.
Sandro Botticelli, workshop of, *Virgin and Child with Saint John the Baptist* (NG 2497), probably *c.*1482–98.	Brown architecture; red lead, lead white, black, vermilion and a little red lake.	Lead soaps and possibly some lead carbonate.[b]	
Hendrick ter Brugghen, *Jacob reproaching Laban* (NG 4164), 1627.	Pale yellow of lemon peel; lead-tin yellow 'type I'.[d]	Lead soaps and basic lead carbonate,[b,d] slightly more carbonate than soaps.[c]	
Lorenzo Costa, *A Concert* (NG 2486), *c.*1485–95.	Highlight on woman's sleeve; lead-tin yellow.[a]	Lead soaps and lead carbonate.[b]	
Gerard David, *Canon Bernardinus de Salviatis* (NG 1045), after 1501.	Yellow highlight from Saint Donation's cloth-of-gold cloak; lead-tin yellow 'type I'.[d]	Lead soaps and lead carbonate,[b] in approximately equal amounts.[c]	
Battista Dossi, ascribed, *Venus and Cupid*, 16th century, Gemäldegalerie, Berlin.	Yellow highlight on cloud; lead-tin yellow.[a]	Lead soaps and basic lead carbonate,[b] in approximately equal amounts.[c]	Drying oil, A/P 0.5.
Karel Dujardin, *Portrait of a Young Man* (*Self Portrait?*) (NG 1680), *c.*1655.	Grey underpaint; lead white, coarse black and red lead. Yellow highlight of the braiding on the sitter's jacket; lead-tin yellow.	Lead soaps only in both samples.[b]	Heat-bodied linseed oil in the yellow highlight, A/P 0.4.
Anthony van Dyck, *Lady Elizabeth Thimbelby and Dorothy, Viscountess Andover* (NG 6437), *c.*1637.	Yellow highlight on Lady Dorothy's gown; lead-tin yellow 'type I'.[d]	Lead soaps and basic lead carbonate.[b,d]	Partially heat-bodied linseed oil, A/P > 1.
Anthony van Dyck, *William Feilding, 1st Earl of Denbigh* (NG 5633), *c.*1633–4.	Yellow highlight on the shot pouch; lead-tin yellow.	Lead soaps.[b]	Heat-bodied walnut oil.
English School, *Wall painting from St Stephen's Chapel*, 1350–63, Palace of Westminster (now British Museum).	Priming layer; red lead.	Lead soaps and basic lead carbonate,[b] more carbonate than soaps.[c]	Drying oil, low azelate.
English School, *The Thornham Parva Retable*, *c.*1335.	Oil mordant beneath gilding on the canopy foliage; earth pigments and red lead.[a]	Lead soaps and basic lead carbonate,[b] more carbonate than soaps.[c]	Drying oil, A/P 0.1.
English School, *The Westminster Retable*, *c.*1260–80.	Orange lining of Saint John's robe, Scene IIIa; red lead.[a]	Lead soaps and basic lead carbonate,[b] in approximately equal amounts.[c]	Whole sample: linseed oil, A/P 1.0. Inclusion only: linseed oil, A/P 0.2.
English School, *Apocalypse Cycle*, 1375–1404, Westminster Abbey Chapter House.	South bay, Arch 3: red lead and a little vermilion.	Lead soaps and basic lead carbonate,[b] more carbonate than soaps.[c]	Partially heat-bodied linseed oil, A/P 0.93.
Fontainebleau School, *Cleopatra* (NG 5762), 16th century.	Yellow highlight on window shutter; lead-tin yellow.[a] The inclusions contain a little Cl in addition to Pb.[a]	Lead soaps and basic lead carbonate,[b] in approximately equal amounts.[c]	Linseed oil, A/P 0.35.
French School, *Portrait of a Man* (NG 947), probably 16th century.	White translucent highlight on gold chain; originally orange, traces of red lead remain.	Lead soaps and basic lead carbonate,[b] in approximately equal amounts.[c]	
French School, *Portrait of a Lady* (*Madame de Gléon?*) (NG 5584), *c.*1760.	Red ground layer; red earth and red lead.	Lead soaps and basic lead carbonate,[b] in approximately equal amounts.[c]	
Garofalo, *A Pagan Sacrifice* (NG 3928), 1526.	Pale yellow of drapery of naked woman; lead-tin yellow.	Lead soaps and lead carbonate,[b] in approximately equal amounts.[c]	
Francisco de Goya, *Portrait of Don Andrés del Peral* (NG 1951), before 1798.	Pinkish-orange ground layer; red lead, lead white and silica.	Lead soaps and basic lead carbonate,[b] more carbonate than soaps.[c]	Heat-bodied linseed oil, A/P 1.3.
Meindert Hobbema, *The Avenue at Middelharnis* (NG 830), 1689.	Yellow highlight on a small tree in the background; lead-tin yellow 'type I'.[d]	Lead soaps in translucent areas.[b] More opaque regions also contain basic lead carbonate[b] and possibly some cerrusite.[d]	Linseed oil, A/P 1.4.
Master of Cappenberg, *Christ before Pilate* (NG 2154), *c.*1520.	Yellow mordant of oil gilding; red lead, lead-tin yellow.[a]	Lead soaps and basic lead carbonate,[b] more carbonate than soaps.[c]	
Master of the Saint Bartholomew Altarpiece, *Saints Peter and Dorothy* (NG 707), 1510.	Yellow from the Virgin's crown, reverse of the panel; lead-tin yellow 'type I'.[d]	Lead soaps and basic lead carbonate,[b,d] more soaps than carbonate.[c]	Linseed oil, A/P 0.6.

Artist, painting title and date	Description of the paint layers containing inclusions	Content of inclusion	GC–MS results; oil type, azelate/palmitate ratio (A/P)
Michele da Verona, *Coriolanus persuaded by his Family to spare Rome* (NG 1214), *c.*1495–1510.	Orange underdress of woman second from left; red lead[d] and some massicot.[e]	Lead soaps and basic lead carbonate[b], possibly some cerrusite.[d] More carbonate than soaps.[c]	Walnut oil, A/P 0.2.
Moretto da Brescia, *Madonna and Child with Saint Bernardino and other Saints* (NG 625), *c.*1540–54.	Yellow highlight from lining of Virgin's cloak; lead-tin yellow 'type I'.[d]	Lead soaps and lead carbonate,[b,d] in approximately equal amounts.[c]	Walnut oil, A/P 0.1.
Moretto da Brescia, *Madonna and Child with Saints Hippolytus and Catherine of Alexandria* (NG 1165), *c.*1538–40.	Red hose of Saint Hippolytus; red lead and vermilion.[a]	Lead soaps and lead carbonate,[b] more soaps than carbonate.[c]	
Daniel Mytens, *Portrait of Charles I*, 1628, Royal Collection.	Red ground layer; red lead and red earth.[a]	Lead soaps and basic lead carbonate,[b] more carbonate than soaps.[c]	
Parmigianino, *The Madonna and Child with Saints John the Baptist and Jerome* (NG 33), 1526–7.	Red of Saint Jerome's cloak; vermilion and red lead.[a]	Lead soaps and basic lead carbonate,[b] more carbonate than soaps.[c]	
Raphael, *Saint Catherine of Alexandria* (NG 168), *c.*1507–8.	Yellow sunlit sky; lead-tin yellow.[a]	Lead soaps and (basic?) lead carbonate,[b] more carbonate than soaps.[c]	Walnut oil, A/P 1.98.
Rembrandt, *Belshazzar's Feast* (NG 6350), *c.*1636–8.	Yellow impasto highlight on Belshazzar's cloak; lead-tin yellow.[a,d]	Lead soaps (little or no lead carbonate).[b]	Linseed oil.
Jacopo Tintoretto, *Portrait of Vincenzo Morosini* (NG 4004), probably 1580–5.	Bright orange paint on sitter's sash; red lead and lead-tin yellow 'type I'.[d]	Lead soaps and basic lead carbonate,[b,d] more carbonate than soaps.[c]	
Paolo Veronese, *The Rape of Europa* (NG 97), 1570s?	Yellow highlight on Europa's pink brocade; lead-tin yellow 'type I'.[d]	Lead soaps and basic lead carbonate,[b,d] more soaps than carbonate.[c]	Walnut oil, A/P 0.6.
Paolo Veronese, *Allegory of Love, I ('Unfaithfulness')* (NG 1318), probably 1570s.	Primrose yellow of the drapery of man on the right; lead-tin yellow 'type I'.[d]	Lead soaps and basic lead carbonate,[b] in approximately equal amounts.[c]	
Paolo Veronese, *Allegory of Love, II ('Scorn')* (NG 1324), probably 1570s.	Highlight on man's drapery; red lead and lead-tin yellow 'type I'.[d]	Lead soaps and basic lead carbonate,[b] more carbonate than soaps.[c]	
Francisco de Zurbarán, *A Cup of Water and a Rose on a Silver Plate* (NG 6566), *c.*1630.	Grey paint of cup; lead white, black and lead-tin yellow.[a]	Lead soaps and lead carbonate,[b] more soaps than carbonate.[c]	

Notes to Table 1
a. Identified by EDX in the SEM
b. Identified by FTIR microscopy
c. The ratio of the peaks at *c.*1400 and *c.*1500 cm^{-1} in the FTIR spectrum was used to estimate the proportion of lead carbonate to lead soaps
d. Identified by XRD
e. Identified by Raman microscopy

Appendix: Preparation of Lead Fatty Acid Soaps

Azelaic, stearic and palmitic acids (or derivatives) are the principal fatty acids detected by GC–MS analyses on paintings and it was therefore decided to concentrate on the lead soaps of these acids. A variety of methods were used to prepare lead carboxylates in the laboratory but the basic strategy was to take a soluble lead(II) salt (lead acetate or nitrate) and to add a solution of the appropriate fatty acid directly.[1] As expected, the resulting lead fatty acid soaps were all extremely insoluble in a variety of solvents,[2] so purification was effected by washing to remove unreacted material and the acid by-product (acetic or nitric acid).

Lead palmitate and stearate were characterised by comparison with FTIR spectra of lead(II) and other metal palmitate and stearate soaps (salts) reported in the literature.[3] EDX analysis confirmed the presence of lead in the soaps and GC–MS demonstrated that the soaps contained palmitate and stearate respectively. The FTIR spectra for the two monocarboxylate soaps are shown in FIG. 5 (middle and lower traces) and the characteristic frequencies listed in Table 2.[4] XRD was not attempted as the d-spacings of the crystalline metal soaps are known to be too high to be detected on the available instrument.[5] In addition, most of the samples prepared appeared to be amorphous.

Lead azelate, prepared in the same manner, was more difficult to characterise, as there is little information available in the literature, and because of the extreme insolubility of the soap.[6] The FTIR spectrum is shown in FIG. 9, with the characteristic frequencies listed in Table 2. EDX analysis again confirmed the presence of lead, and GC–MS the presence of azelate. An elemental analysis was also obtained: Calculated for $PbC_9H_{14}O_4$: C, 27.48; H, 3.59; Pb, 52.67%. Found: C, 26.53; H, 3.26; Pb, 52.67%. While the results for the lead azelate were in good agreement with a 1983 study of lead(II) dicarboxylates,[7] further confirmation of the formation of lead azelate was sought. As with the palmitate and stearate soaps, the high d-spacings precluded powder XRD.[8] Using hydrothermal synthesis,[9] the Chemistry Department at the University of Aberdeen prepared crystals of lead azelate suitable for single crystal XRD.[10] The FTIR spectrum of the material prepared by this method matched that of the lead azelate derived from lead nitrate and azelaic acid produced at the National Gallery. The crystal structure, solved by the EPSRC National Crystallography Service,[11] confirmed that the sample was indeed lead azelate and showed that it has a 3D polymeric network structure, similar to the polymeric or polynuclear structures that have been found for the majority of lead carboxylates studied (including those of the monocarboxylic acids).[12]

Appendix notes and references

1 R.C. Mehrotra and R. Bohra, *Metal Carboxylates*, London 1983, Chapter 2; M.S. Akanni, E.K. Okoh, H.D. Burrows and H.A. Ellis, 'The thermal behaviour of divalent and higher valent metal soaps: a review', *Thermochimica Acta*, 208, 1992, pp. 1–41.

2 E. Rocca and J. Steinmetz, 'Inhibition of lead corrosion with saturated linear aliphatic chain monocarboxylates of sodium', *Corrosion Science*, 43, 2001, pp. 891–902; *CRC Handbook of Chemistry and Physics,* 68th edn, ed. R.C. Weast, Boca Raton 1987, pp. B100–1; W. Brzyska and H. Warda, 'Preparatyka I Wlasciwosci Alkanodikarboksylanów Olowiu (II)', *Rudy I Metale Niezelazne*, 28, 1983, pp. 204–8; Mehrotra and Bohra 1983, cited in note 1.

3 M.A. Mesubi, 'An Infrared Study of Zinc, Cadmium and Lead Salts of some Fatty Acids', *Journal of Molecular Structure*, 81, 1982, pp. 61–71; L.J. Bellamy, *The Infrared Spectra of Complex Molecules,* Vol. 1, 2nd edn, Cambridge 1975; N.P.G. Roeges, *A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures*, Chichester 1994; R. Matura, 'Divalent metal salts of long chain fatty acids', *Journal of the Chemical Society of Japan*, 86, 1965, pp. 560–72.

4 Mesubi 1982, Bellamy 1975, Roeges 1994 and Matura 1965, all cited in note 3; Brzyska and Warda 1983, cited in note 2.

5 Rocca and Steinmetz 2001, cited in note 2; F. Lacouture, M. Francois, C. Didierjean, J.P. Rivera, E. Rocca and J. Steinmetz, 'Anhydrous lead(II) heptanoate', *Acta Crystallographica Section C – Crystal Structure Communications*, 57, 2001, pp. 530–1; M.-C. Corbeil and L. Robinet, 'X-ray powder diffraction data for selected metal soaps', *Powder Diffraction*, 17, 2002, pp. 52–60; Akanni et al. 1992, cited in note 1.

6 Brzyska and Warda 1983, cited in note 2; A.J. Appleby and J.E.O. Mayne, 'Corrosion inhibition by the salts of the long chain fatty acids', *Journal of the Oil and Colour Chemists' Association*, 50, 1967, pp. 897–910.

7 Brzyska and Warda 1983, cited in note 2.

8 Brzyska and Warda 1983, cited in note 2.

9 M.R.St J. Foreman, M.J. Plater and J.M.S. Skakle, 'Synthesis and Characterisation of Polymeric and Oligomeric Lead(II) Carboxylates', *Journal of the Chemical Society, Dalton Transaction*, 2001, pp. 1897–1903; M.R.St J. Foreman, T. Gelbrich, M.B. Hursthouse and M.J. Plater, 'Hydrothermal Synthesis and Characterisation of Lead(II) Benzene-1,3,5-tricarboxylate $[Pb_3BTC_2]\cdot H_2O$: A Lead(II) Carboxylate Polymer', *Inorganic Chemistry Communications*, 13, 2000, pp. 234–8.

10 M. John Plater, University of Aberdeen, and Mark R. St J. Foreman, University of Reading.

11 Thomas Gelbrich, EPSRC National Crystallography Service, University of Southampton.

12 Foreman et al. 2001 and Foreman et al. 2000, both cited in note 9; Rocca and Steinmetz 2001, cited in note 2; Lacouture et al. 2001, cited in note 5; Akanni et al. 1992, cited in note 1; J.-M. Rueff, N. Masiocchi, P. Rabu, A. Sironi and A. Skoulios, 'Structure and Magnetism of a Polycrystalline Transition Metal Soap – $Co^{II}[OOC(CH_2)_{10}COO](H_2O)_2$', *European Journal of Inorganic Chemistry*, 2001, pp. 2843–8; J.-M. Rueff, N. Masiocchi, P. Rabu, A. Sironi and A. Skoulios, 'Synthesis, Structure and Magnetism of Homologous Series of Polycrystalline Cobalt Alkane Mono- and Dicarboxylate Soaps', *Chemistry – A European Journal*, 8, 2002, pp. 1813–20.

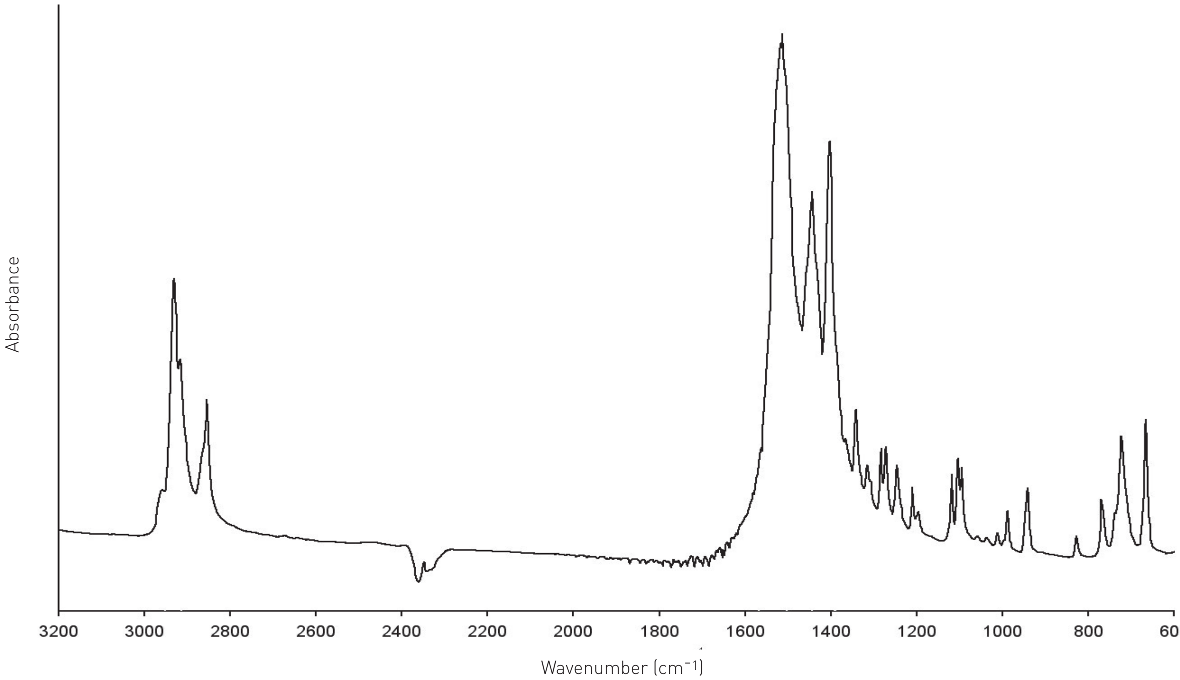

FIG. 9 FTIR spectrum (3200–600 cm^{-1}) of a standard sample of lead azelate prepared during this study.

TABLE 2 Characteristic infrared frequencies (cm^{-1}) for lead soaps of palmitic, stearic and azelaic acids in the 4000–700 cm^{-1} region (vs: very strong; s: strong; m: medium; w: weak; d: doublet)

Assignment	Lead palmitate	Lead stearate	Lead azelate
asymmetric C–H stretch of CH_3– ; CH_2–	2955 (w); 2918 (vs)	2955 (w); 2918 (vs)	2959 (w); 2931 (s)
symmetric C–H stretch of CH_3– ; CH_2–	2871 (w, shoulder); 2849 (vs)	2871 (w); 2849 (vs)	2914 (s); 2854 (s)
asymmetric COO– stretch (doublet)	1541 (s), 1513 (s)	1540 (s), 1513 (s)	1517 (vs)
C–H bend	1473 (m), 1462 (m)	1473 (m), 1462 (m)	
symmetric COO– stretch	1419 (m)	1419 (m)	
C–H bend (?)	1407 (m, shoulder)	1402 (m, shoulder)	1444 (vs)
symmetric COO– stretch			1403 (vs)
evenly spaced progression of bands – long chain n-alkyl chain rocking and twisting of –CH_2–	1349 (w), 1333 (w), 1315 (w), 1295 (w), 1274 (w), 1253 (w), 1232 (w), 1210 (w), 1189 (w)	1347 (w), 1333 (w), 1318 (w), 1299 (w), 1281 (w), 1263 (w), 1244 (w), 1225 (w), 1206 (w), 1187 (w)	
	930 (w)	930 (w)	1364 (w), 1341 (m), 1315 (w), 1283 (m; d), 1271 (m; d), 1245 (m), 1209 (w), 1118 (m), 1103 (m), 1094 (m), 988 (w), 941 (m), 827 (w), 769 (m), 722 (m)
–CH_2– rock (torsion)	731 (w), 719 (w)	731 (w), 719 (w)	