Color changes and chemical reactivity in seventeenth-century oil paintings
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White Hazes and Surface Crusts on Dark Oil Paint Films

**Abstract** – In this chapter, the origin of whitish hazes and crusts that develop on the surface of dark paint layers, leading to unwanted changes in texture and color, is examined, as well as the implications for conservation. Examples include seventeenth-century oil paintings by Dutch Masters from museum collections and historic interiors. Although the dark paint mixtures slightly vary in composition – apart from bone black and carbon black pigments, they contain earth pigments, chalk, red and yellow lakes and smalt –, the chemical processes that take place in these paint layers are largely comparable. In some cases, the whitening was found to be caused by degradation of chalk-based yellow or red lakes in original glazing surface layers. In other cases, the whitening arises from migration of mobile paint components to the surface. The white surface degradation layers were found to all exist primarily of lead soap crystals, lead chlorides, lead/potassium sulfates and calcium oxalates. These deterioration products have formed as a result of the development and migration of lead soaps and potassium soaps inside the paint layers, and subsequent interaction at the paint surface with the environment (dust and dirt particulates, micro-organisms and air pollutants). The lead soaps result from dissolution of lead white present in an underlying layer. Potassium may come from various pigment sources: smalt, earth pigments or substrates of lake pigments. This chapter provides valuable insight into the degradation and migration processes typical of these dark paints.

**Introduction**

**Surface Deterioration and Surface Crusts**

White bloom on chocolate, weathered stone facade, blackened silverware, … just to name some common examples from the world around us that are the result of compositional changes of the surface of materials involving the formation of a skin or thin film on an object. These deterioration processes have to do with/are caused by extractable compounds that separate out or migrate to the surface of the object, and/or interaction of the object with atmospheric gases or particles at the interface. A process of migration followed by precipitation at the surface can also be seen in the formation of mineral deposits or coatings on geological materials such as rocks, soils, sediments, (mine) tailings and wood surfaces [Hammerstrom and Smith 2002; Dorn 2007]. Capillary action draws pore water containing soluble salts to the surfaces, where they evaporate to form salt crusts that may react further by interaction with the environment.

Similar leaching, corrosion and encrusting processes take place in works of art. Surface deposits and crust formations of inorganic salts, mainly carbonates, sulfates, chlorides, nitrates, phosphates and oxalates, have been extensively reported on metal objects like copper and bronze [Scott 2002], ancient glass [Woisetschläger 2000; Lefèvre
2002], marble statues and fresco paintings [Cariati 2000]. The salts formed depend on the material compositions and the environment in which the objects have been kept. Studies of surface deposits on (unvarnished) modern oil (and alkyd) paintings have identified free, saturated fatty acids in the efflorescence or related compounds such as fatty acid salts (lead palmitate and stearate) and paraffinic hydrocarbons substances, obviously originating from the binding media of paint or ground layers [Williams 1988; Ordonez and Twilley 1997; Skaliks 1999; Van den Berg 2002a]. Analyses of the paint layers of some of the works of art affected suggest the strong influence of certain binding media, pigments and painting techniques [Skaliks 1999]. Certain dark colors appear more susceptible than others. Black carbonized products, Kassel earth, ultramarine, vermilion and alizarin lakes retard the drying of the oil and, in addition, are highly oil-absorbing. It is also thought that the higher porosity of the film promotes the migration of mobile paint constituents. The fatty acid precipitates are mechanically removable or with solvents, but usually the efflorescence or bloom returns after a number of years, since the migration continues until a new equilibrium is reached. Occasionally, inorganic salts have been detected on the surfaces of modern paintings, lead chlorides [Ordonez and Twilley 1997] and sulfur-containing lead compounds [Van den Berg 2002a]. Lead sulfide is also known to be formed at the surface of lead white paints by interaction with \( \text{H}_2\text{S} \) in the polluted London atmosphere of the late-nineteenth century [Carlyle and Townsend 1990].

Studies on surface deterioration in seventeenth-century oil paintings usually apply to particular pigments. The blackening of vermilion and the fading of organic colorants, both surface degradation phenomena, are caused by light-induced photochemical reactions. Whitening/blanching has also been attributed to the use of hygroscopic pigments rich in silicates (green earth, ultramarine, smalt, chalk and ochres) [Groen 1988; Epley 2000]. However, we should also consider the role of free fatty acids and metal (lead) soaps in the formation of (insoluble) surface deposits, as well as reactions with anionic sources in the environment to form inorganic salts such as sulfates and carbonates, comparable to the surface deposits encountered on modern paintings and metal and glass objects as discussed above. Recently, surface crusts on deteriorated smalt layers were examined that show similarities in formation to glass deterioration [Spring et al. 2005].

Until now, the formation of white hazes and crusts on dark-brown and black paint films in seventeenth-century oil paintings has not been examined in great detail, despite the widespread occurrence and the strong visual impact they impose to the painting. This may have to do with the fact that the color black is less appealing compared to blue or red tones and more difficult to categorize in terms of artistic intention, and that such thin layers on the paint surface are analytically challenging due to limitations of the analytical techniques. During the recent investigations of the whitening of bone black (see Chapter 3), we encountered other whitening problems related to dark paint films. The nature and origin of these white surface crusts will be discussed, as well as consequences for treatment.
Chapter 4

Whitening — Nomenclature

In conservation and conservation science, many terms have been used to describe a whitish appearance on paintings: blanching, blooming, efflorescence, chalking, clouding, sweating, flooding/flotation, crazing, fading, bleaching, hazing, whitening, crystallization, micro-fissures, micro-cracking, micro-voids, blushing, mould etc. [Hess 1951; Skalik 1999]. Most of them are quite specific and relate to the mechanism of the whitening. Fading or bleaching refers to discoloration/color loss of the pigment in particular of organic pigments such as the red and yellow lakes that are light-sensitive and are susceptible to photochemical degradation [Saunders and Kirby 1994]. Blanching means a physical break-up of the paint surface. Micro-fissures, crazing, micro-cracking, micro-voids also imply a physical break-up of the paint. A good example is ultramarine sickness, where the ultramarine paint appears grayish while the ultramarine particles themselves have retained their blue color.  

This phenomenon is often ascribed to the presence of micro-fissures at the paint surface that scatter the light, owing to a physical break-up of the paint medium/matrix [Groen 1993]. The term blooming is used to describe the process of migration of extractable components in the paint and their deposition at the surface. It is typically applicable to white precipitates of organic origin such as free fatty acids, waxes or metal soaps. Efflorescence is more specific for crystalline (inorganic) deposits on the surface, water-soluble salts. Mildew or mold (fungus) refers to the growth of micro-organism on the surface. Chalking implies breakdown of binding medium due to pigment interaction. Sweating refers to free fatty acids and soaps that come out of the paint. Transferred images or ghost images may develop when extractable components from the paint deposit on the inside of protection glass that is placed in front of the painting. Since the exact mechanism of the whitening is often not known, it is safer and clearer to use a more general term to describe the surface phenomenon, such as whitening, hazing or white surface depositions (exudates/accretions), precipitates or crusts (encrustations).

Selection of the Paintings

Ten case studies will be discussed in detail (see Table 4.1): two paintings by Pieter de Grebber and one by Salomon de Bray from the Oranjezaal, a painted ceiling from the Johan de Witt House, painted ceilings from the Trippenhuis, Rembrandt’s Portrait of a Standing Man from Kassel, as well as Rembrandt’s Homer, Simeon’s Song of Praise, a painting by Philips Wouwerman, and a portrait by Frans Hals from the Royal Picture Gallery Mauritshuis. These ten paintings vary in display and restoration history. The paintings from the Oranjezaal ensemble have always been displayed in the same room, under relatively constant environmental conditions, and have similar, known restoration histories that comprise very few interventions. The painted ceiling from the Johan de Witt House has also stayed relatively untouched/undisturbed. It has been neither varnished nor overpainted. In contrast, the painted ceilings from the Trippenhuis have

1 Although there are also occurrences where the pigment has itself lost its color under acidic conditions, see also Chapter 2, footnote 56.

2 In transferred images mainly water soluble sodium soaps are detected [Skaliks 1999].
been covered with many layers of monochrome overpainting, that were partly removed in the 1980s. The painting of *Homer* in the Mauritshuis suffered fire damage in the past, after which it was reduced in size. Here, the whitening of the dark paint layers could have been caused by exposure to heat from a probable fire. This painting is also twice lined. Rembrandt’s *Portrait of a Standing Man* in Kassel has been the subject of earlier studies [Van der Weerd et al. 2002a], but it has been re-examined here. This painting has undergone several, severe restoration treatments in the course of time, including lining. Rembrandt’s *Simeon’s Song of Praise* and Wouwerman’s *Departure from the Stable*, also from the Mauritshuis, painted on panel show less extreme display and restoration records. Likewise, Hals’ *Portrait of Jacob Olycan* has gone through regular cleaning cycles. In nine of the paintings, the composition is severely compromised by the formation of a whitish haze or crust on the surface of the dark areas. Since the whitening is mainly confined to the dark areas in the pictures (also best observable in dark areas), a strong influence of the composition of these dark medium-rich paints is suggested. They were found to contain bone black or carbon black mixed with earth pigments, smalt and red and yellow lakes. The discolorations of the ceilings in the Trippenhuis do not relate to dark areas, but to the blue skies. However, we added them to the selection because of their overlap in composition and degradation behavior, especially with the *Homer*. All the paintings were recently restored, which required a better understanding of the whitening phenomena. Insoluble crusts had formed on the surfaces that didn’t dissolve during cleaning with regular organic solvents. When investigating the whitened paint surfaces with the naked eye, the different whitening phenomena looked very similar. Depending on the degree of deterioration, the whitening manifested as superficial haze or as real crust. Chemical analysis was carried out to characterize the white surface deposits and to clarify the underlying causes that have led to the whitening. Paint samples were examined using light microscopy (LM), scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX), Fourier transform infrared microscopy (FTIR), Raman microscopy, and direct temperature resolved mass spectrometry (DTMS). The combination of specular reflection FTIR imaging and SEM-EDX was particularly helpful, since FTIR imaging enabled the distinction between strong absorption bands of phosphates, sulfates, carbonates, oxalates and carboxylates characteristic of the different white products, while SEM-EDX gave insight in their morphology and elemental compositions. In some cases, only one or two cross-sections were examined, in other cases more samples were allowed and could be studied. Although the degree of deterioration and paint compositions of these objects differ, we will see that the chemical processes and degradation products show many similarities, resulting in a more general understanding of the reactivity of these oil paints. We will first describe the examination results for each painting separately, and then try to categorize the different whitening phenomena and propose a reaction model for the formation of typical insoluble surface encrustations on dark paint layers.
Table 4.1 List of paintings examined

- Pieter de Grebber, *Part of the Triumphal Procession with Spoils of War*, (Oranjezaal, Huis ten Bosch Palace, No. 24), 1648, oil on canvas, 385 x 210 cm

- Pieter de Grebber, *The Ascension of Frederik Hendrik into Heaven*, (Oranjezaal, Huis ten Bosch Palace, No. 22), 1650, oil on panel, 385 x 515 cm

- Salomon de Bray, *Part of the Triumphal Procession with Musicians*, (Oranjezaal, Huis ten Bosch Palace, No. 26), 1649, oil on canvas, 385 x 210 cm

- Unknown artist(s), Painted ceiling with panel imitations (Johan de Witt House, The Hague, room 1.12), 1652-55, oil on panel

- Rembrandt van Rijn, *Portrait of a Standing Man*, (Staatliche Museen Kassel, inv. no. 239), 1639, oil on canvas (lined), 199 x 123.5 cm

- Rembrandt van Rijn, *Homer*, (Mauritshuis, inv. no. 584), 1663, oil on canvas (lined), 107 x 82 cm

- Rembrandt van Rijn, *Simeon’s Song of Praise*, (Mauritshuis, inv. no. 145), 1631, oil on oak panel, 61 x 48 cm

- Philips Wouwerman, *Departure from the Stable*, (Mauritshuis, inv. no. 215), 1655-65, oil on oak panel, 43 x 59 cm

- Frans Hals, *Portrait of Jacob Olycan (1596-1638)*, (Mauritshuis, inv. no. 459), 1625, oil on canvas (lined), 125 x 98 cm

- Unknown artist(s), Painted ceilings with hunting scenes with skies and birds, (Trippenhuis, Amsterdam, corridors and stairwells), 1660-62, oil on panel

**EXPERIMENTAL**

**SAMPLE PREPARATION**

Samples were selected with the stereo-microscope and embedded in Technovit 2000 LC mounting resin, a one-component methacrylate that polymerizes under visible blue light (Heraeus Kulzer, Germany). Samples prepared in the Conservation Studio of the Mauritshuis were embedded in Easy Sections (England) using Poly-pol PS230 polyester mounting resin with M.E.K.-peroxide hardener (Poly-Service, Amsterdam). After initial grinding using silicone carbide (SiC) paper, the surface was dry polished using Micro-Mesh® Sheets (Regular type, grades 1500 thru 12000, Micro-Surface finishing products.
In the following sections, the examined paintings will be described, including manifestation of the whitening, painting technique, display conditions, restoration history, chemical analysis, and conservation issues.

Triumphal Procession with Spoils of War (1648) by Pieter de Grebber from the Oranjezaal

The Triumphal Procession with Spoils of War (No. 24) painted by Pieter de Grebber is part of the mid-17th-century paintings ensemble in the Oranjezaal (The Hague, Royal Palace Huis ten Bosch). The unified decorative/pictorial scheme in the room glorifies the life of stadholder Frederik Hendrik (Fig. 4.1.1). The series of Triumphal Processions, nine canvas paintings in total by different artists, cover the lowest level of the room. This painting by De Grebber is positioned next to the windows and must have been often exposed to direct sunlight in the past, which might have triggered some light-induced fading and color changes of the paint layers. It has always stayed in the same room with...
White hazes and surface crusts on dark oil paints

Fig. 4.1.1 Pieter de Grebber, *Part of the Triumphal Procession with Spoils of War*, (Oranjezaal, Huis ten Bosch Palace, No. 24), 1648, oil on canvas. Overall, pair of boots showing light reflections and detail of the painting showing the degraded surface layer.

Fig. 4.1.2 Light microscopic images of cross-section HTBS 24x43 from thick highlight in boots and corresponding SEM images and EDX maps.
minimal interventions: the painting has not been lined and has undergone no more than three cleaning interventions in the course of time, including the recent restoration (see Chapter 2).\(^3\) Like all the canvases in the Oranjezaal, this canvas has been prepared with a high-quality light-beige colored ground by the primer François Oliviers (see also Chapter 2). During the recent restoration and technical investigation, it was observed that the dark brown, leather boots of the boy at the far right are affected by a whitened surface layer (Fig. 4.1.1). Although shiny leather boots are expected to give some strong reflections of the light (Fig.4.1.1), in this case, the paint surface looks degraded and the whitening effect seems unintentional. This is quite dramatic for the pictorial illusion, since the boy is situated in a dark/shadow area of the painting, and the unintended lightening brings the boots forward in the composition. The whitening is not random, but seems to be related to the final brushstrokes, since it follows the modeling in the boots. In addition, the red coat of the same boy has suffered from blackening of vermilion (upper part) and fading and graying of a red glaze (lower part), as a result of photochemical reactions.

Two samples were collected from the whitened boots, one from a thick brushstroke from a now white highlight, and the other from a grayish haze in a mid-tone area. The samples were prepared as cross-sections and examined using LM, FTIR imaging and SEM-EDX.

The light microscopic image of the cross-section from the highlight (HTBS 24x43) reveals a thick whitish translucent layer (20-50 μm) over a dark-brown paint layer (Fig. 4.1.2). The ground is missing in this sample. The dark-brown underpaint contains rather coarse bone black, fine red earth, chalk, umber, a little lead white and dispersed lead. The bone black is intact here, and is not affected by the whitening phenomenon as described in Chapter 3. The whitish upper layer mainly consists of calcium carbonate, with some very small additions of red earth, carbon black, calcium sulfate and lead-tin yellow. The FTIR image and spectrum of this layer demonstrate a strong absorption band around 1420 cm\(^{-1}\), characteristic of (calcium) carbonate group \(\text{CO}_3^{2-}\). EDX primarily detects calcium (see calcium map Fig. 4.1.2). The backscattered electron images reveal a densely packed, low scattering (dark gray) biogenic calcium carbonate layer, in which some microfossil structures (chamber walls of foraminifera) are recognizable (Fig. 4.1.2). It is also observed that the paint is broken up at the surface, which induces scattering of the light at the surface and thus adds to the whitened appearance on the painting. The few bright, strongly back-scattering particles in the chalk layer represent the lead-tin yellow particles; they overlap with the ‘hot spots’ (high intensities) in the tin map.

In the second cross-section (HTBS 24x44), collected from the gray haze, the complete layer build-up is present. The cross-section shows, in succession, a thick, beige-colored ground consisting of lead white and umber, a dark-brown underpaint

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\(^3\) The restoration of the Oranjezaal ensemble was initiated by the State Building Agency (Rijksgebouwendienst (Rgd), The Hague) and carried out between 1998-2001 by a large team of conservators under supervision of Anne van Grevenstein, Limburg Conservation Institute (SRAL, Maastricht). Technical investigations of the paintings were continued in the MOLART (1998-2002) and De Mayerne (2002-2006) projects.
that contains bone black, fine red earth, umber, chalk, a little lead white and dispersed lead, and a gray-brown finishing layer (15-35 μm) that appears lighter with a more granular structure towards the surface (Fig. 4.1.3). Apart from some carbon black, red and brown earth, the surface layer contains a high amount of calcium carbonate/chalk. Calcium is the major element detected in this layer by EDX. The composition is comparable to that of the surface layer in the first cross-section, but more pigmented and darker in tone. The FTIR image of the carbonate group ν(CO$_3^{2-}$) at c. 1416 cm$^{-1}$ indicates the strong presence of this moiety in the upper layer (from calcium carbonate/chalk) and in the ground layer (from lead white) (Fig. 4.1.3). In the FTIR spectra of the top layer, absorption bands were also observed at c. 1634 cm$^{-1}$ and c. 1318 cm$^{-1}$ which closely correlate to reference data of calcium oxalate (Fig. 4.1.3) [Cariati 2000]. Usually the most characteristic feature for calcium oxalate sharp at c. 1320 cm$^{-1}$. The FTIR image of the oxalate group reveals that it is mainly concentrated at the surface (Fig. 4.1.3). This chalk-rich paint layer seems to be comparable with calcareous substrates, such as stone and fresco surfaces, where calcium oxalates form typical alteration layers. The occurrence of calcium oxalate crusts/films is often being associated with the intervention of micro-organisms, but oxalates can also be formed by oxidation of organic materials [Cariati 2000]. Both possibilities are plausible/conceivable in this case. Furthermore, SEM-EDX analysis gives evidence for the presence of another deterioration product at the paint surface that adds to the grayed surface appearance of the boots. The backscattered electron images demonstrate fine, highly scattering amorphous material near the surface. EDX detected lead and a high amount of chloride in these areas (Fig. 4.1.4). The Pb : Cl ratio is in the order of 1 : 2. This lead chloride compound could not be characterized further. On the basis of the element ratio, it is possible that cotunnite (PbCl$_2$) has formed, but this needs to be confirmed with additional chemical analysis. It is thought that the lead comes from an underlying layer, the brown underpaint, that also contains some lead white and dispersed lead, or the lead white-based ground. Chloride is often associated with lead white, probably introduced during the production process. The lead chloride compound might have been mobilized by moisture transport through the layers. Most lead chlorides, like cotunnite, are a little soluble in water.

It appears that the surface layer was originally a translucent glaze layer, applied over a brown underpaint to create modeling in the leather boots. Loose black brushstrokes (still intact) are used in the shadow parts, while probably different brown shades have been used for the lighter areas and highlights. The paint surface now looks degraded. Physical break-up of the paint layer, leading to micro-cracks and voids in the surface that scatter light, and the formation of deterioration products, among which

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4 The lead chloride did not yield a Raman spectrum: only the signal of calcium carbonate of the matrix showed up. However, the question is whether Raman is the suitable technique in this case, since a Raleigh filter cuts off all scattering under 200 cm$^{-1}$, and Raman bands of cotunnite are to be expected at 202, 169, 158 cm$^{-1}$ [Bouchard and Smith 2003]. Phosgenite, conversely, would have shown an intense Raman band at 1861 cm$^{-1}$ [Frost et al. 2003].

5 During the manufacture of lead white, strips of metallic lead were placed in porous earthenware pots, over weak acetic acid (vinegar) in sheds with fermenting (horse) manure that produces heat and CO$_2$ [Gettens et al. 1993]. Horse manure contains 25% NaCl.
calcium oxalate and lead chloride, at the surface have contributed to the whitened appearance of the paint. The glazing layer contains a high amount of calcium carbonate/chalk. The question remains whether the calcium carbonate/chalk was used as filler to make a translucent (light) brown glaze, or is more likely the substrate of a now degraded yellow dyestuff (see also discussion in the main text). These chalk-based yellow lakes were known as ‘pinks’ or ‘schiet-yellows’ in the seventeenth century. Depending on the type of yellow dye, they existed in yellow-green and yellow-brown varieties. Although stylistically a (brown) yellow lake is to be expected, the possibility of a now deteriorated brazilwood should also be considered, since this inferior red organic colorant is also found precipitated on alumina/chalk substrates [Saunders and Kirby 1994]. HPLC analysis was not successful in detecting an organic dyestuff. The presence of a yellow lake, in particular, is often difficult to prove, since the yellow organic dyestuff has usually faded away to nothing visible and nothing detectable by HPLC as a result of photochemical reactions. However, previous studies have shown that its use can be indicated by a high concentration of calcium/chalk), while the aluminum may be barely detectable by EDX (as is also the case here). Brazilwood is also very light-sensitive and may be hardly measurable by HPLC. In comparison, analysis of a paint sample from a green leave in this painting -collected from the crown (wreath) of leaves pictured on the head of the kneeling, central figure- also identified the presence of chalk throughout the layer, in addition to the gray-blue earth pigment vivianite. Here again, HPLC analysis was not successful in detecting the organic coloring matter, but in this case the chalk must definitely come from a chalk-based yellow lake, since there is no other yellow pigment present in this layer, and the admixture of a yellow pigment is required to make a green color. Likewise, the surface layer in the lower shadow area of the red coat of the same boy appears whitened and degraded, but originally must have been a red or red-brown glaze used for final modeling of the shadows, applied on top of a red-brown underpainting with red earth and carbon black. The layer contains calcium sulfate and

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7 HPLC analysis with both array and fluorescence detection was carried out by Maarten van Bommel, Netherlands Institute for Cultural Heritage Amsterdam 2007. No (yellow or red) dye components could be detected, except for a trace of ellagic acid, i.e. tannin. The presence of tannin is usually associated with the extraction of red dyestuffs (esp. cochineal and madder) from textile shearings. Tannin has also been identified in some red glaze samples from other Oranjezaal paintings (analyses carried out by Jan Wouters 2003): 11A1 (in combination with cochineal and brazilwood) and 3A2 (in combination with Mexican cochineal and brazilwood) [Clarke et al.]. So, maybe a mixture of dyestuffs has been used in this case, including brazilwood. Another possibility is that tannin comes off with a yellow dye that self has completely faded away. Ellagic acid might be present in yellow dyewoods, in small amounts [Hofenk de Graaff 2004]. Thus, the detection of ellagic acid might give some indication of the presence of a deteriorated dyestuff, but is certainly no solid proof.


9 HPLC analysis was carried out by Maarten van Bommel, Netherlands Institute for Cultural Heritage Amsterdam 2007. A yellow dyestuff was only successfully identified in one of the paintings in the Oranjezaal, in the Triumphal Procession with Elephant and Paintings by Van Thulden, where a green leaf was sampled that had been shaded from the light by the frame (See Chapter 2). SEM-EDX analysis of a cross-section of the same area detected primarily calcium in the yellow particles, and only minor traces of aluminium, indicating the yellow dyestuff was adsorbed on a chalk substrate.
White hazes and surface crusts on dark oil paints

Fig. 4.1.4 SEM backscatter and EDX spectrum of a lead chloride product deposited at the paint surface.

Fig. 4.1.3 FTIR imaging data of cross-section HTBS 24x44.

carbonate $1403 \text{ cm}^{-1}$  phosphate/silicate $1049 \text{ cm}^{-1}$  oxalate $1634 \text{ cm}^{-1}$
calcium carbonate particles, possibly as substrates of a now faded brazilwood and/or other red lake pigment, in addition to fine red earth.\textsuperscript{10}

It can be concluded that a degraded glaze layer applied on top of the dark-brown paint layer is responsible for the now whitened surface appearance of the boots. Although the exact composition and color shade of the original surface layer stays unclear, the fact that it involves an original layer is crucial information, not only for future treatment, but also for the mental picture.

\textbf{Painted Ceiling ‘The Ascension of Frederik Hendrik into Heaven’ (1650) by Pieter de Grebber from the Oranjezaal}

Pieter de Grebber also painted one of the four vaulted portions of the ceiling representing \textit{The Ascension of Frederik Hendrik to Heaven} (No. 22) as part of the decorative/pictorial scheme glorifying the life of Stadholder Frederik Hendrik. The ceiling painting is executed \textit{in situ} directly on the wooden planks of the vault, which, like most of the wooden elements in the Oranjezaal, were given a chalk-glue preparatory layer followed by a light-gray priming layer consisting of lead white in oil with small additions of earth pigment and carbon black. During the recent technical investigation of the painted vault, it was noted that the dark-brown hair of a cherub portrayed in the sky is affected by a white efflorescence, which has caused unintended highlights in the dark curls (Fig. 4.2.1).

With the naked eye, the whitening looks very similar to the phenomenon of the whitening of bone black as described in Chapter 3. Surface examination with the light microscope (at 100-200x magnification) of a paint sample collected from a whitened area prior to embedding shows light-brown striations integrated in the dark paint film. Part of the paint sample was prepared as cross-section for analytical studies with LM, FTIR imaging and SEM-EDX in an attempt to characterize the nature and origin of the white efflorescence further.

The light microscopic image of the cross-section reveals a warm light-brown underlayer, followed by the dark brown-black surface layer of which the uppermost part (approx. 10 μm) and a few clusters within the layer are discolored (Fig. 4.2.2). The preparatory layers are missing in this sample. The discolored zones in the dark surface layer exhibit a strong fluorescence in UV illumination (Fig. 4.2.2), and high scattering in the SEM backscatter image (Figs. 4.2.3 and 4.2.4), which contrasts with the rest of the dark paint. The dark layer is composed of medium-sized round particles of bone black and a brown earth pigment; dispersed lead is detected throughout the layer by EDX. Bone black can be distinguished from other carbon blacks by its high content of calcium phosphate mineral. The FTIR image of the phosphate group (PO\textsubscript{4}\textsuperscript{3−}) at c. 1050 cm\textsuperscript{-1} overlays the dark layer. EDX detected the elements calcium and

\textsuperscript{10} When examining the painting with UV light during treatment, areas of the red coat exhibited a strong fluorescence, an indication of the presence of a (degraded) organic red lake glaze. HPLC analysis was not carried out in this case.
phosphorus in the black particles, which further confirms the presence of bone black. In the discolored zones, however, hardly any bone black was measured. It seems that the bone black particles themselves have stayed intact, since they don’t show any sign of the whitening phenomenon that occurred in other paintings from the Oranjezaal (see Chapter 3), and that another underlying cause is responsible for the whitening in this case. The discolored areas were further characterized with SEM-EDX. The morphology and high scattering of these zones imply the formation of new mineral phases that have accumulated at and near the surface in the open pores of the paint structure. The more amorphous areas appear less dense (grayer), whereas, probably as a result of remineralization processes, the three-dimensional concentric, lobed structures look whiter and denser at the outside and dark and empty inside. Lead is the only metal detected in these strongly scattering regions. The lead map shows the abundance of this element at the surface of the black paint, and smaller concentrations throughout the layer. In addition to lead, EDX also detected some sulfur in these areas, which seems to be consistent with the sulfate band at around 1100 cm$^{-1}$ $\nu$(SO$_4^{2-}$) that was recognized in the FTIR spectra. This implies part of the deposit is present in the form of a lead sulfate (anglesite). It can also be seen in the backscatter images that small bright, discrete particles (of a few hundred nm in diameter) are dispersed throughout the black layer in the matrix between the bone black particles. The fine horizontal striations they form in some places are interpreted as gradients of diffusion/migration (Fig. 4.2.3). The presence of these fine particles accords/correlates with the low concentrations of lead detected throughout the layer. The agglomerations of these lead-rich particles at the surface of the paint are likely the result of their migration through the layer towards the surface, where they accumulated and remineralized giving the paint a translucent-whitish appearance.

The question remains where the lead-containing particles come from. The dark brown layer does not seem to contain any lead white or other lead-containing pigment, and the amount of lead is considered too excessive to be just from an added drier (see Discussion). They most likely originate from the lead-white containing underlayer. In the light microscopic image, the light-brown underlayer looks transparent in several places throughout the layer. It contains lead white, earth pigment, and a little black pigment. Examination of this layer with SEM-EDX demonstrates a high degree of saponification of the lead white. The SEM backscatter images reveal a few large, coarse particles of lead white with a few distinct, smaller white particles, but the main part of this layer has a less dense (grayer) and more amorphous appearance (Fig. 4.2.3). The gray halos (of metal soaps) around the highly scattering well-defined particles indicate that the lead white is being transformed into lead soaps (see also Chapter 5). The small particles dissolve more easily in the oil medium than the larger particles, since they are more in contact with the reactive oil-derived constituents. Lead soap formation in the light-brown underlayer is also evident from FTIR imaging which shows a prominent absorption band at $\approx$1519 cm$^{-1}$, characteristic of the asymmetric lead carboxylate group $\nu$(COO). The symmetric carboxylate band overlaps with the carbonate band at around 1400 cm$^{-1}$. Absorption peaks for the C-H bonds, typical of the aliphatic chain of the carboxylate $\nu$(CH$_2$) and $\nu$(CH$_3$), manifest in the 2900 cm$^{-1}$ region.
Chapter 4

Fig. 4.2.1 Pieter de Grebber, *The Ascension of Frederik Hendrik into Heaven*, (Oranjezaal, Huis ten Bosch Palace, No. 22), 1650, oil on panel.

Fig. 4.2.2 Light microscopic images of cross-section from whitened hair showing fluorescent zones at the surface.
Fig. 4.2.3 SEM backscatter image of dissolution and saponification of lead white in the lower layer. Horizontal rims of lead throughout the dark paint layer suggest migration of lead soaps towards the surface.

Fig. 4.2.4 SEM backscatter image showing partially mineralized lead soap structures at the surface of the dark paint.
Chapter 4

It can be concluded that lead soaps, developed in the lower lead-white containing layer, have migrated to the dark-brown upper layer, where they are deposited at and near the surface. The surface deposit probably consists of mineralized lead soaps, part of the lead soaps having converted to lead sulfate (anglesite) after reaction with sulfur compounds from the atmosphere. This material has a light-brownish tone and its presence explains the whitened appearance of the dark paint observed in several places of the dark hair. The position of this painting in the room, at more than eight meters height, and its construction on wood may have created optimized humidity conditions that promote(d) the formation and migration of lead carboxylates towards the surface.

‘PART OF THE TRIUMPHAL PROCESSION WITH MUSICIANS’ (1649) BY SALOMON DE BRAY FROM THE ORANJEZAAL

The Triumphal Procession with Musicians (No. 26) by Salomon de Bray was also commissioned by Amalia van Solms for the Oranjezaal. It is part of the series of classical triumphal processions on the lowest level of the decorative scheme. Due to its position in the room, it has captured less light compared to De Grebber’s Triumphal Procession discussed earlier. The minimal interventions together with mild environmental conditions have kept the painting in relative good (physical) condition. The painting is not lined, and, like the other canvases in the Oranjezaal, is prepared with a uniform, light-beige colored ground applied by the primer François Oliviers (see also Chapter 2). The recent restoration offered the opportunity for close study of the painting. Several areas in this painting demonstrate graying of the paint surface that has resulted in loss of modeling and detail, especially the dark cloak of the old man appears whitened and spotty (center right) (Figs. 4.3.1 and 4.3.2). As compared with the Triumphal Procession by De Grebber, a deteriorated calcium sulfate-based red or red-brown glaze layer with small additions of red earth and carbon black was also identified using SEM-EDX and FTIR imaging in this painting in a shadow area of the red clothing of the child (lower right corner) (see also Chapter 2). In the clothing of the other figures, the degraded areas were found to contain the blue earth pigment vivianite, and thus were originally blue or green areas, but these issues fall outside the scope of this chapter (see also Chapter 2). Here, we will just focus on the investigation of the graying of the dark cloak.

At first sight, the grayed surface appearance of the dark cloak suggests/resembles a deteriorated smalt layer. Examination of the paint surface with the stereo-microscope (up to 20x magnification) revealed that, instead of a continuous layer, the surface layer consists as little, cloudy islands, in which some coarse black pigment particles are recognizable, on top of the brown underpaint (observations L. Speelers). A cross-section was collected from the grayed mantle (next to the horse’s nose), and investigated using LM and SEM-EDX to get a better understanding of the paint composition and the original color.

The paint cross-section reveals the complete layer build-up: a little ground, a reddish underpaint (appears light-brown on the painting), followed by several dark
brown paint layers containing large carbon-based black particles, fine red earth, some lead white/lead tin yellow particles, dispersed lead, in addition to a large amount of chalk. On top of the brown paint, a grayish translucent layer (5-20 μm) is present in which semi-transparent particles and some carbon-based black pigment are discernible (Fig. 4.3.3). SEM-EDX demonstrates that this glaze layer consists mostly of calcium carbonate/chalk. The high concentration of chalk is visualized in the calcium map in Fig. 4.3.3. There is also a small concentration of dispersed lead detected throughout the layer. Not only do the backscatter images reveal physical break-up of the paint layer at the surface, but also a few highly scattering deposits at the surface of the glaze layer (Fig. 4.3.3) contribute to the whitened appearance of the paint surface. EDX analysis shows these deposits are rich in lead and arsenic. Lead may come from an underlying brown layer where some lead white/lead-tin yellow/dispersed lead was detected. The source of arsenic is not entirely clear; we suggest a contamination in the paint or a very small addition of orpiment, an arsenic sulfide, that has converted to arsenic oxide.

From the analytical results, it is evident that the grayish surface layer was originally a translucent glaze layer applied by the artist to create modeling and a special color effect in the cloak of the old man. The glaze layer contains a high amount of calcium carbonate. Like in the Triumphal Procession by De Grebber, here again, the question is whether the calcium carbonate was used as filler to body the paint to make a translucent (light) brown glaze, or more likely as substrate of an organic dyestuff (see also the discussion in the main text). In the case of a chalk-based yellow lake, or pink or schiet-yellow as they were called in that time, the resulting was probably a greenish color, since a yellow lake glaze on top of a dark brown or black underlayer would have resulted in a green hue. Historical treatises also suggest the construction of a green color for draperies by glazing one color over another color. For example, Marshall Smith described an olive color comprising white, blue-black and bone black, glazed with brown pink [Kirby and Saunders 1998]. On stylistic grounds, however, a red lake glaze or a mixture of red and yellow are also possible options.

In conclusion, apart from fading of a possible yellow dyestuff, a physical break-up of the paint layer at the surface that induces light-scattering, and the formation of a thin, uneven surface deposit rich in lead and arsenic give the paint a grayed appearance. Hence, it is clear that more studies are needed to be able to identify degraded organic (yellow) lakes, which may clarify these kinds of ageing phenomena. Thus, the exact composition and color shade of the original surface layer remains unknown for now.

**Painted Ceiling (1652-55) from the Johan de Witt House in the Hague**

The Johan de Witt House on the Kneuterdijk in The Hague was built by the architect Pieter Post allegedly around 1650. Johan de Witt, raadspensionaris (Grand Pensionary) of Holland, lived in the house for a couple of years till his death in 1672. The ceilings on the first floor in this classicistic mansion are decorated with trompe l’oeil paintings applied directly on the wooden planks. These unique ceilings also date from the
Fig. 4.3.1 Salomon de Bray, *Part of the Triumphal Procession with Musicians*, (Oranjezaal, Huis ten Bosch Palace, No. 26), 1649, oil on canvas.

Fig. 4.3.2 Degraded paint surface of the dark cloak of the old man in Fig. 4.3.1.
White hazes and surface crusts on dark oil paints

Fig. 4.3.3 Light microscopic images and corresponding SEM images and EDX maps showing degraded calcium-rich surface layer.
middle of the seventeenth century, around the same time as the Oranjezaal, and show comparable paint compositions and degradation behaviors. In one room, the small gray cabinet at the yard-side, the dark-painted shadow edges of (the painted frames that are part of) the panel imitations on the ceiling are distorted by a white surface deposition, that is particularly abundant reducing the illusion of depth considerably (Fig. 4.4.1). Since this painted ceiling has been neither varnished nor overpainted, it provides a unique case study. This ceiling was shielded by a lowered ceiling consisting of gypsum panels since the 1960s. When the gypsum panels were taken off, more holes in the wooden beams showed up, which suggests, although this is not solid proof, that the ceilings had been covered already before the 1960s. During the renovation of the building in 2003, the ceilings were re-discovered and restored.11

With the naked eye, the whitening looks very similar to the phenomenon of the whitening of bone black as described in Chapter 3. It appears randomly distributed over the paint surface. Samples were taken from both degraded zones and areas that still appear black.12 Examination with the light microscope (at 100-200x magnification) of the surface of unembedded paint samples collected from the whitened areas reveal rather thick, semi-translucent whitish veils on the surfaces (like snow flakes that have fallen down, but are not pressed together yet) suggesting more/rather a surface deposit than a change within the layer. The surface of a paint chip was also examined with the electron microscope, that demonstrated the growth of highly scattering, plate-like (lead-rich) structures on the paint surface (Fig. 4.4.2). Part of the sample material was prepared as cross-sections for analytical studies using LM, FTIR imaging, Raman microscopy, SIMS and SEM-EDX in an attempt to characterize the composition of the black paint layer and the white efflorescence further. Furthermore, isolated samples of the white efflorescence and of the black paint were analyzed using single-point transmission FTIR and DTMS.

The various cross-sections from the whitened and apparently unaffected black areas show similar layer build-ups and paint compositions. They reveal successively a chalk ground, a light-gray paint consisting of lead white and some very fine carbon black, and a dark brown paint that contains bone brown/black, umber, some lead white and dispersed lead (Fig. 4.4.3). The binding medium of the dark paint is found to be linseed oil (P:S=1.6-1.7). Mass peaks are observed at $m/z$ 60, 73, 129, 171, 185, 213, 241, 256 and 284 that are characteristic of palmitic acid and stearic acid and their EI fragments. These EI fragments (e.g. $m/z$ 129) are detected in three different events suggesting the fatty acids are present in different forms, free, ester and metal bound [Keune 2005b]. A small peak is present at $m/z$ 152, a fragmentation ion from azelaic acid. In the higher temperature region of the total mass spectrum, the typical peak pattern of the pyrolysis products of the oil paint network is present, with mass peaks at e.g. $m/z$ 91, 105. In the inorganic fraction at the end of the measurement at

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11 Johan de Witt House is property of the State Building Agency (Rijksgewendienst (Rgd), The Hague). The restoration of the ceilings was carried out in 2003 by Edwin Verweij | Verweij Office for Architectural Paint Research and Conservation (Amsterdam) and a team of conservators.

12 The surface degradation seems to be restricted to the black areas. The gray and white tones in the painted panel imitations were samples sampled for comparison, but no surface depositions were noticeable in those samples.
White hazes and surface crusts on dark oil paints

high temperatures, some lead is detected at m/z 206-208, and phosphorus typical of bone black at m/z 62 (P) and 124 (P₄). Bone black can be distinguished from other carbon blacks by its high content of calcium phosphate matter. The FTIR image of the phosphate group (PO₄³⁻) at c.1050 cm⁻¹ overlays the dark layer (Fig. 4.4.3). EDX detects the elements calcium and phosphorus in the black particles, which further confirms the presence of bone black. Raman microscopy only reveals broad carbon bands in the black layer at c.1580 and c.1340 cm⁻¹. The phosphate bands of bone black usually do not show up in Raman spectra, probably because the hydroxyapatite is too amorphous (see also Chapter 3). The bone black is intact, and does not seem to be affected by the whitening phenomenon as described in Chapter 3. Another chemical process is therefore responsible for the whitening observed.

In the light microscopic images, translucent-whitish surface depositions on top of the dark brown upper paint layer are visible in cross-sections from both affected (white) and apparently unaffected areas. They are fluorescent in UV light and strongly scattering in SEM backscatter mode (Figs. 4.4.3). There are also some black dirt particles trapped/incorporated in the surface crust. The SEM images illustrate that the deposits are thicker (up to 25 μm) and much more defined (probably more crystallized) in cross-sections from the whitened areas compared to those from the apparent intact areas where they appear thinner and more amorphous. The SEM backscatter images of cross-sections from whitened/affected areas illustrate well-developed lamellar arrangements in the surface deposit (Figs. 4.4.3, 4.4.5 and 4.4.6). The ordered structures appear light-gray in the SEM images; they are strongly scattering, but are probably less dense and more organic in nature compared to the lead white pigment particles in the underlying light gray paint layer, that appear brighter in the SEM. The crust is clearly incorporated in the paint structure. Elemental analysis of the surface deposit using EDX reveals that it mainly contains lead and carbon. The map for lead shows high concentrations of this element in the surface crust and in the light gray paint, which contains lead white; the map registers minor amounts of lead in the black layer. FTIR imaging on the cross-sections indicates the presence of lead carboxylates/soaps in the white surface deposit as seen by a strong absorption band at c.1539 cm⁻¹ associated with the carboxylate group O=C-O. A plot of the distribution of this band over the cross-section demonstrates a high concentration of carboxylates in the area/part of the white surface deposit (Fig. 4.4.3). Supplemental analysis by single-point FTIR transmission carried out on a scraping of the white surface material confirms that the bulk of the surface deposit consists of lead carboxylates/soaps. The FTIR spectrum with bands for the carboxylate group at c.1539 cm⁻¹ and c.1409 cm⁻¹ (asymmetric and symmetric stretch vibrations) and for the C-H bonds of the aliphatic chain at c.2933 cm⁻¹ and c.2855 cm⁻¹ (asymmetric and symmetric stretch vibrations) closely correlates to FTIR reference data of pure lead stearate and lead palmitate (Fig. 4.4.4) [Robinet and Corbeil 2003]. This suggests that

13 The morphology and analytical data of the lead soap deposits are largely comparable with white crystals on the surface of a late-nineteenth century canvas painting by the Dutch artist S.C. Bosch-Reitz that was recently examined [Keune et al. 2006].
Fig. 4.4.1 Unknown artist(s), Painted ceiling with panel imitations (Johan de Witt House, The Hague, room 1.12), 1652-55, oil on panel (left) and dark shadows affected by whitening (right detail).

Fig. 4.4.2 SEM image showing plate like lead soap crystals in plain focal view growing on the paint surface.
Fig. 4.4.3 Analytical images data of cross-section from whitened area, UV light microscope (upper left), SEM backscatter (upper right) and FTIR imaging (lower left and right).

Fig. 4.4.4 FTIR transmission spectrum of lead soap crystals.
the efflorescent soap material is primarily composed of (saturated) mono-carboxylic fatty acid soaps. The mono-carboxylics are considered the most mobile fractions in the aged oil paint film that can migrate through the paint and deposit/accumulate at the surface. The presence of high amounts of palmitic and stearic acid soaps is also reflected in the DTMS data. The DTMS spectra of the white precipitate comprise mass peaks for palmitic and stearic acid at $m/z$ 256 and 284 (ratio 5:2) and their EI products, that basically desorb in one event (scans 50-60) indicating the fatty acids are present in metal-bound form. At higher scans (> scan 60), the isotope patterns for lead at $m/z$ 206-208 are the main peaks detected. Evidence of the presence of minor amounts of dicarboxylic fatty acid soaps is given from the presence of ions at $m/z$ 348-350, fragments deriving from decarboxylation of lead azelate [Keune 2005b].

Apart from a high amount of lead, EDX detected minor traces of other elements in the deposition that are consistent with those found in studies of airborne particulate dirt (Al, Mg, P, K, Ca, Cl, S, Si, Fe), which accords with the trapped blackish (dirt) particles observed in the light microscopic images. Furthermore, the presence of a small quantity of a lead sulfate mineral phase is suggested by the successive analytical techniques. In some areas of the crust, Raman spectroscopy clearly reveals a small, sharp peak at 977 cm$^{-1}$, attributable to lead sulfate (anglesite) [Burgio and Clark 2001]. This is further supported by the presence of the mass peak $m/z$ 64 noticed in the DTMS spectra, indicative of $S_2/\text{SO}_2$, as well as the unknown/unresolved FTIR absorption bands in the 1100-1050 cm$^{-1}$ region from the S-O stretching vibrations of the sulfate group $\nu(\text{SO}_4^{2-})$. The formation of lead sulfate is likely to be a result of interaction of lead carboxylates with atmospheric sulfur. There are no indications for the presence of lead carbonates in the crust.

Comparable to the cross-section from the De Grebber ceiling, very small, strongly scattering discrete particles (of a few 100 nm in diameter) are noted in the matrix of the dark paint layer in the backscatter images (Figs. 4.4.5 and 4.4.6). These particles are probably lead-based, since these areas are enriched in lead, as shown by EDX. In addition, the dark layer also seems to contain a little lead white. Some dissolution of lead white is expected in the medium-rich dark paint layer, since bone black and earth pigments are known to be highly oil-absorbing, although this is not evident from the SEM images. It is also possible that an excess of lead drier was used in the dark paint, since bone black is not only highly oil-absorbing due to its porous structure and large surface area, but also has anti-oxidant properties and retards the drying of the oil (see also Chapter 3). The amount of lead at the surface, though, is considered too much to come just from an added drier. Moreover, the admixture of umber in the dark paint, that has good drying properties, makes an excess of lead drier less necessary and thus less likely. The lead white present in the lower, light gray layer is likely to be another important source for lead/the formation of lead soaps. Although the SEM images show a rather compact lead white layer, the layer appears disrupted at the interface with the dark layer and there are some grayish, amorphous areas visible around the lead white particles that suggest some dissolution of the pigment. Part of the lead soaps has already clustered within the dark paint layer and seems to have disrupted the
White hazes and surface crusts on dark oil paints

Fig. 4.4.5 SEM backscatter detail of the deposition of lead soap crystals at the surface.

Fig. 4.4.6 SEM backscatter detail of the deposition of lead soap crystals at the surface.
paint layer in some places, the greater part, however, has migrated to the top of the paint and formed a deposit at the paint surface (Figs. 4.4.5 and 4.4.6). Since the ceiling was untouched for centuries, the metal carboxylates had time to develop and accumulate at the surface. Moreover, the surface is here not covered with a varnish layer, which has allowed the deposits to grow/develop more freely on the surface.

The fact that the lead soap deposit is clearly integrated with the paint structure has consequences for the cleaning of the paint surface. When trying to remove the white material mechanically with a scalpel knife or other tool - the lead soaps were not sensitive to solvent-cleaning -, one has to be very careful not to ruin the paint layer underneath. It is only possible to reduce the deposit, but not totally remove it without damaging the original paint. During the recent treatment of the ceiling, the white deposits were locally saturated with varnish – Paraloid B72, a vinyl acetate derived polymer- to make them less disturbing to the viewer.

‘PORTRAIT OF A STANDING MAN’ (1639) BY REMBRANDT VAN RIJN FROM THE STAATLICHE MUSEEN KASSEL

The whitening of the dark paint in Rembrandt’s Portrait of a Standing Man (inv. nr. GK 239) from the Staatliche Museen Kassel (Fig. 4.5.1) has been the subject of earlier studies [Van der Weerd et al. 2002]. It was re-examined within the context of this research, since the whitening could be associated with the use of bone black in the dark paint and might be comparable with the whitening phenomenon of bone black as described in chapter 3. This painting has a turbulent storage and restoration history [Brammer 1987; Brammer 1992; Hermesdorf and Schnackenburg 1992]. Dissolution and swelling of overpaint and varnish layers was noticed that could be ascribed to an old treatment with the Pettenkofer regeneration method. The glue-paste lining that was applied in the nineteenth century was replaced by a wax-resin lining during the last treatment in 1989/90. Removal of the many layers of old varnish and overpaint revealed a damaged and cupped paint underneath, particularly disturbing in the black of the clothing and the dark warm-gray background. This is likely to be the result of aggressive cleaning in the past and the very humid climate of the old gallery room where the painting was kept. In addition, large passages of the black of the clothing as well as most of the shadow and half-shadow areas in the background - where the monochrome underpainting is uncovered- are affected by a whitening effect of the paint surface making these originally dark areas appear rather pale. Surface examination of the paint with the stereo-microscope revealed that the lower parts of the brush-work/paint texture still appear dark, whereas the edges of the cupped paint and the higher, pasteuze paint appear white. During cleaning tests by the restorer Hans Brammer in the 1980s, before the last restoration, the reason for a large overpaint in the shadow zone below the man’s right arm became clear when removal of the overpaint revealed a thin whitish layer at the surface of the dark brown paint layer [Brammer 1987]. A cross-section from the deepest shadow area was also taken and examined with LM by Hans Brammer at that time. We
White hazes and surface crusts on dark oil paints

Fig. 4.5.1 Rembrandt van Rijn, *Portrait of a Standing Man*, (Staatliche Museen Kassel, inv. no. 239), 1639, oil on canvas (lined).

Fig. 4.5.2 Light microscopic images of cross-section from whitened shadow area showing discoloration.
re-examined this same cross-section using LM, FTIR imaging, Raman spectroscopy and SEM-EDX.

The cross-section shows the complete layer build-up of the original paint structure and the many layers of varnish and overpaint, applied during the successive past restoration treatments. The vertical crack in the middle of the cross-section, filled with varnish, evidences the severe cupping of the paint. The canvas is prepared with a double ground consisting of a red-brown layer containing mainly red earth, followed by a light-gray layer that contains lead white and some fine lamp black, a typical Amsterdam ground and often seen/found in Rembrandt’s paintings. On top of the ground is one single dark paint layer in which black and a few fine red pigment particles are discernable in a dark-brown matrix. This layer corresponds to the monochrome underpainting, the dead-coloring (*doodverf*), that is exposed/uncovered in large areas of the painting varying from red-brown to dark gray-brown tones [Brammer 1992: 223]. The light microscopic image shows the dark paint layer appears lighter/more transparent towards the surface (the uppermost 5 μm).

FTIR imaging and SEM-EDX analysis demonstrate that calcium carbonate is the main component present in the dark paint layer. The FTIR spectrum shows a strong, broad absorption band at 1430 cm⁻¹, representative of the carbonate group ν(CO₃²⁻). EDX confirms the presence of calcium. The FTIR image of the carbonate group reveals a homogeneous distribution of this group in the dark paint and the whitened surface. The FTIR image also highlights the lead white in the second ground layer, since the carbonate peaks of lead white and chalk overlap. Apart from a little earth pigment (fine red earth), alumina-substrated red lake and dispersed lead, there is also some bone black present in the dark paint layer. EDX detected the elements calcium and phosphorus in the black particles, which are associated with bone black. Bone black can be distinguished from other carbon blacks by its high content of calcium phosphate mineral, hydroxyapatite. In the previous study by Van der Weerd et al., the presence of calcium carbonate in the layer was interpreted as a thermal degradation product of hydroxyapatite. However, with more knowledge now on the composition of bone black (see Chapter 3), it is understood that the mineral phase, calcium phosphate, is very stable at high temperatures and that it does not convert to calcium carbonate. Of course, bone black usually contains minor amounts of calcium carbonate (and calcium sulfate), in addition to calcium phosphate, but calcium carbonate is present here in much larger proportions than bone black. Hence, the calcium carbonate is more likely to be an original component of the paint and not a degradation or by-product. The presence of calcium carbonate in large quantities in surface layers is often interpreted as residual substrate of a now degraded yellow lake/schiet-yellow, or a deteriorated brazilwood lake, that was also used in combination with chalk substrates. The organic dyestuff has usually faded away as a result of photochemical reaction and is therefore difficult to prove. However, calcium carbonate may also have been used in its own right as colorless extender to add body and translucency to the dark brown paint.¹⁴ We have said earlier

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in this text that the dark brown paint layer is in fact the dead-coloring paint that has been left uncovered here to function as a shadow. Chalk has previously been noticed in brown sketch layers in other paintings by Rembrandt (e.g. *Simeon's Song of Praise*), as well as in several paintings in the Oranjezaal. It is also sometimes encountered in dark-colored glaze layers, mixed with other pigments such as earths, in Rembrandt's technique [Bomford et al. 2006]. It is also suggested that the addition of chalk improves the brushability of the sketch/dead-coloring layer.

Furthermore, the FTIR spectra of the dark paint layer reveal, in addition to the large carbonate peak around 1430 cm\(^{-1}\), smaller features at c.1640 cm\(^{-1}\) and c.1320 cm\(^{-1}\). Imaging these peaks indicates them to correspond to the degraded surface of the dark paint layer. These bands were previously attributed to distortions in the reflected light spectra of chalk owing to an alteration of the calcium carbonate [Van der Weerd et al. 2002]. Attribution to oxalates seemed highly unlikely at that time. However, the combination of a strong, broad peak at c.1640 cm\(^{-1}\) \(\nu\) \(\text{COO}^-\) and a weak, sharp one at c.1320 cm\(^{-1}\) \(\nu\) \(\text{COO}^-\) is very characteristic of calcium oxalates [Cariati 2000]. In the meantime, the presence of oxalates has also been found in other surface crusts on paintings where it was confirmed using additional techniques such as XRD and GC-MS that detects the oxalate ion [Sutherland et al. 2005; Spring et al. 2005; Higgitt et al. 2005]. Such chalk-rich paint layers seem to be comparable with other calcareous substrates, such as marble statues and fresco paintings, where calcium oxalates are commonly observed on the surface as deterioration products. The occurrence of calcium oxalate crusts/films is being associated with the intervention of micro-organisms as well as with the oxidation of organic materials [Cariati 2000]. Physical break-up of the paint layer at the surface, as seen in the SEM backscatter images, leading to micro-cracks and voids that scatter light, also adds to the whitened appearance of the paint. This seems to correspond with Brammer's observations of the affected paint surface that he describes as 'Bindemittelkrepierungen' (physical break-up of binding medium/blanching).

SEM-EDX analysis also demonstrates the presence of another deterioration product, a lead chloride compound, at the paint surface that might contribute to the whitened surface appearance of the shadow area. The backscattered electron images reveal an inhomogeneous film of finely dispersed, highly scattering amorphous material near the surface (Fig. 4.5.3). Lead and a high amount of chloride were detected in these areas by EDX in the proportion of 1 : 2. On the basis of the element ratio, it can be deduced that cotunnite (PbCl\(_2\)) has formed, but this should be confirmed with additional chemical analysis. The backscattered electron images give evidence of a diffusion process of lead chloride, formed at the interface between the dark paint layer and the underlying ground layer, towards the paint surface. Fig. 4.5.4 illustrates the presence of tiny, light-gray amorphous particles at the border area between the

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15 Analyses carried out by the author (e.g. HTBS 6x4, 26A9, 27x23).
17 We tried to confirm the presence of oxalates at the surface of the dark paint layer with Raman spectroscopy. Unfortunately, we could only detect the Raman band at 1089 cm\(^{-1}\) characteristic of the calcium carbonate group.
18 See footnote 4.
dark brown paint and the upper lead white-containing ground, where also small concentrations of chloride were detected by EDX and that are similar/identical in morphology as the particles at the surface. Chloride is often associated with lead white, probably introduced during the production process.\(^\text{19}\) It is also possible that the chloride originates from the dark paint itself (or is a contaminant from the environment) and interacts with the lead white ground at the boundary of the two layers. It can also be seen that there is a stream/flow of particles along the vertical crack. The lead chloride particles are thought to be mobilized by moisture transport and to be redistributed near the surface. Most lead chlorides, like cotunnite, are a little soluble in water. In the SEM images, it is also noticed that the lead chloride is primarily concentrated at the surface near cracks, which appears to be related with the surface observation that mainly the edges of the cupped paint are affected by whitening.

It can be concluded after re-examination of the cross-section, that the originally dark brown, exposed underpaint contains large quantities of chalk (as filler, or possibly as substrate of a yellow/red dyestuff) mixed with smaller amounts of bone black, alum-substrated red lake and earth pigment. The layer originally must have appeared much more translucent owing to the presence of that much chalk. Physical break-up of the paint surface in addition to the formation of calcium oxalates and lead chlorides at the surface are held responsible for the whitening effect. It is uncertain whether previous restoration treatments and/or poor storage conditions in the past have played a role in the now whitened appearance of the dark paint.

‘Homer’ (1663) by Rembrandt van Rijn from the Royal Picture Gallery Mauritshuis

Rembrandt’s painting depicting the blind Homer dictating his verses (inv. nr. 584) (Fig. 4.6.1) was commissioned by the Sicilian collector, Don Antonio Ruffo from Messina [Noble et al. 2006].\(^\text{20}\) Originally, the painting was much larger, including two scribes.\(^\text{21}\) The painting was severely damaged, most likely during the earthquake of 1783, probably as a result of a fire that broke out, which destroyed the palace of the Ruffo family in Messina. The canvas has been cut down on all sides. The glue-lining, visible on the back of the picture was probably applied shortly before 1900, when it was treated by the German restorer, Alois Hauser. On the X-ray photograph it can be seen that in between the lining canvas and the original canvas is an additional support fabric: an open weave, gauze-like (Italian?) fabric suggesting that the picture may have been restored for the first time in Italy shortly after it was damaged in the 1783 earthquake.\(^\text{22}\) The lower

\[^{19}\text{See footnote 5.}\]
\[^{20}\text{Ruffo ordered three paintings from Rembrandt, all depictions of celebrated Fig. 4. from classical antiquity: Aristotle with a Bust of Homer (1653), Alexander the Great (1661) and Homer (1663). The Aristotle is now in the collection of the Metropolitan Museum of Art in New York. The Alexander the Great is now lost.}\]
\[^{21}\text{All that remains of only one of them are two fingers holding a pen at the lower right.}\]
\[^{22}\text{This intermediate canvas is glued to the original canvas with a mixture of chalk and red earth bound in oil thickened with beeswax (DTMS analysis March 2006, FOM-AMOLF).}\]
White hazes and surface crusts on dark oil paints

Fig. 4.5.3 SEM backscatter image showing lead chloride product along crack (left) and at surface (right).

Fig. 4.5.4 SEM backscatter image showing interface between upper lead white ground and dark paint.
section of the painting is in poor condition: a great deal of paint has been lost and what remains is darkened and deformed. This is probably the result of extended exposure to heat from the fire. Furthermore, a rather thick, insoluble whitish deposit or crust covers most of the dark areas in the painting, including the dark background, Homer's garment, and his cap, to the extent that much of the original contrast and the color are diminished (Fig. 4.6.2). The crust does not follow the composition, but spreads across adjacent forms. The question is whether the crust is also the result of the fire. The nature and origin of the whitening was examined together with the conservator during the recent treatment in the Conservation studio of the Mauritshuis (2004-2006) to help with making decisions on the cleaning of the painting. Additional analysis of a scraping of the white crust was carried out using single-point FTIR transmission spectroscopy. The binding media of the paint and ground layers were also analyzed using DTMS.

A cross-section taken from a black brushstroke in the garment at the lower section of the picture (MH 584x04), which now appears degraded and grayed, shows the complete layer build-up of the original paint structure with the whitish crust at the surface (Fig. 4.6.3). The preparatory layers consist of a double ground: a thick orangy chalk-rich lower ground with some additions of earth pigment, followed by a thinner, gray/brown upper layer that contains lead white, some chalk, earth pigment (umber) and black pigment. In this sample the lead white in the upper ground appears completely saponified in the backscattered electron image, from which it can be concluded that the ground must now appear darker than it originally was. On top of the ground, a thin translucent brown layer is visible in normal light that is interpreted as the sketch layer. This layer is composed of organic brown -possibly Kassel earth\(^2\)-, red earth, silicate particles (and lake pigments?). Separated by what is interpreted as an intermediate varnish, the thick first modeling layer of the drapery was applied that is rich in smalt, lake(s), bone black, dispersed lead, in addition to a lot of evenly dispersed fine particles of red earth.\(^2\) The smalt is very discolored, as shown by the low levels of potassium in the particles measured with SEM-EDX. On top of the drapery layer is a black layer.

\(^2\) The technical examination and treatment were carried out by Petria Noble in the Conservation Studio of the Mauritshuis 2004-2006.

\(^3\) Sample preparation and light microscopy using a Nikon Optiphot-2 microscope were done by Petria Noble in the Mauritshuis Conservation department.

\(^4\) XRD analysis was also tried on an isolated sample of the crust, but, unfortunately, this measurement didn't turn out to be successful: there were only some weak broad bands visible in the spectrum after two hours measuring; it was not enough material for XRD and/or the crust components are too amorphous. With thanks to Kees Goubitz, University of Amsterdam, Department of Crystallography, April 2007.

\(^5\) Kassel earth was also identified in a sample of the blackened paint in the lower damaged shadow area of the left sleeve using DTMS. There, the DTMS spectra reveal C26-34 fatty acids at \(m/z\) 396, 410, 424, 452, 480 and 508, and C46-62 wax esters at \(m/z\) 676, 704, 732, 760, 788, 816, 844, 872 and 900. The presence of long chain saturated fatty acids as well as long chain wax esters are characteristic of Kassel earth pigment [Languri 2004].

\(^6\) A thin fluorescent, medium-rich layer that overlies the sketch layer is interpreted as an intermediate varnish, probably applied when the painting was sent in unfinished state to Italy in 1661, to the collector/patron Don Ruffo, for approval [Noble et al. 2006: 16-17]. This layer appears in many of the cross-sections.
corresponding to a final black brushstroke that primarily consists of bone black. Bone black can be distinguished from other carbon blacks by its high content of calcium phosphate mineral. The FTIR image of the 1053 cm\(^{-1}\) band, indicative of the phosphate group (PO\(_4^{3-}\)), reveals an even distribution of this peak in the black layer (Fig. 4.6.3). EDX detected the elements calcium and phosphorus in the black layer, which further confirms the presence of bone black. The bone black is intact, and does not seem to be affected by the whitening phenomenon as described in Chapter 3. The bone black layer is covered with a thick, white crust (approx. 10-15 μm) that has a light-grayish fluorescence in UV light.

The backscattered electron images show deposits of fine powdery, strongly scattering particles concentrated at and near the paint surface. EDX detected the elements lead, potassium, sulfur and calcium in the crust (Fig. 4.6.4). The EDX maps of lead, potassium and sulfur demonstrate the abundance of these elements at the surface (Fig. 4.6.5). A complex mixture of several mineral phases is suggested by the FTIR transmission spectrum of a scraping of the white precipitate (Fig. 4.6.6). Strong absorption bands in the 1200-1050 cm\(^{-1}\) region may be attributed to S-O stretching vibrations of the sulfate group ν(SO\(_4^{2-}\)) [Derrick et al. 1999]. In addition, the FTIR spectrum indicates some carbonate salts among the components present in the crust. The bands at c. 1390 cm\(^{-1}\) ν(CO\(_3^{2-}\)) and c.680 cm\(^{-1}\) ν(CO\(_3^{2-}\)) are indicative of lead carbonate, whereas the band at c.1429 cm\(^{-1}\) can be ascribed to calcium (and potassium?) carbonate. Furthermore, the band present at c.1560 cm\(^{-1}\) can be assigned to the asymmetric stretch vibration of potassium soaps ν(COO). Calcium oxalates also contribute to the FTIR spectrum of the white crust with absorption bands at c.1637 cm\(^{-1}\) ν(COO), c.1320 cm\(^{-1}\) ν(COO), and c.780 cm\(^{-1}\) ν(OCO).\(^{28}\) Usually the most characteristic absorption for calcium oxalates is the sharp peak at c. 1320 cm\(^{-1}\). In the FTIR imaging spectra, the oxalate bands also show up at 1637 and 1320 cm\(^{-1}\). The FTIR image of the oxalate group at 1637 cm\(^{-1}\) reveals it is concentrated at the surface (Fig. 4.6.3). The concentration of calcium detected by EDX is relatively low compared to lead and potassium, indicating that calcium oxalate is only present as minor element in the crust. The presence of calcium oxalate would certainly add to the insoluble character of the crust.

Cross-sections from other whitened areas in the painting reveal surface crusts on top of brown or black translucent tones that consist of mixtures of varying amounts of bone black, lakes and earth pigments, in addition to a lot of smalt. For example, a cross-section taken from a black area in the cap (MH 584x05), shows a blackish paint layer that consists of smalt, bone black, yellow lake and finely dispersed red earth, built up in one or two applications, on top of what appear to be residues of the second ground layer. In this sample, the lower ground is missing. SEM-EDX analysis and FTIR imaging demonstrate similar compositions of the white crust material to that found on the black brushstroke in the garment (discussed above). Supplemental analysis by Raman microscopy confirmed the presence of lead potassium sulfate-containing deterioration

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\(^{28}\) Two forms of oxalate are commonly found. The infrared bands of the monohydrate phase, whewellite, are seen at 1622, 1319 and 779 cm\(^{-1}\); the dihydrate form, weddellite, has absorption bands at 1641, 1329 and 781 cm\(^{-1}\) [Cariata et al. 2000].
products in the crust. The Raman spectrum reveals a small, sharp peak at 982 cm\(^{-1}\), which closely correlates to reference data of lead sulfate (anglesite) PbSO\(_4\), and potassium sulfate K\(_2\)SO\(_4\) that exhibit strong bands at respectively 979 cm\(^{-1}\) and 983/4 cm\(^{-1}\) [Burgio and Clark 2001]. Calcium sulfate would have shown a band at higher wavenumber, at 1006 cm\(^{-1}\). Since the position at 982 cm\(^{-1}\) lies in between the reference data of the pure compounds, it may even point to the formation of complex/composite/double (sulfate) salts of lead and potassium rather than simple lead sulfates or potassium sulfates. In comparison, small quantities of palmierite (K\(_2\)Pb(SO\(_4\))\(_2\)) and anglesite (PbSO\(_4\)) have been found as degradation products associated with medieval stained glass windows [Sterpenich 2002]. From the backscattered electron images, it is clear that the crust is intimately bound with the paint, appearing as dense, finely dispersed material clustered at and near the surface and containing primarily lead, potassium and sulfur. Fig. 4.6.7 illustrates a concentrated area of the fine scattering grains in the thick crust (up to 20 μm) in a cross-section taken from the left sleeve (MH 584x56) in backscatter mode. A Raman spot measurement of this area detected again a band at 982 cm\(^{-1}\) associated with lead sulfate and/or potassium sulfate. A few aluminum-silicate particles are incorporated in the crust, that is likely to be trapped dirt (Fig. 4.6.8). The backscattered electron images show how the deterioration products accumulate in the matrix between the pigment particles and diffuse/spread/grow through the paint layer towards the surface (Fig. 4.6.9). Identification of the crust in samples from other degraded dark areas in the painting, see Table 4.2, consistently show the degradation products to contain the elements lead, potassium, sulfur and calcium suggesting comparable complex mixtures of several mineral phases: mostly lead and potassium compounds, sulfates, carbonates and carboxylates, as well as various calcium compounds, oxalates and carbonates.\(^{29}\)

The complex composition of the surface crust suggests that several chemical processes are taking/have taken place in the paint layer. Migration/diffusion of lead and potassium from the lead white- and smalt-rich underlying paint layers, implied by the SEM images and analytical data, appear to play an important role in the formation of the surface crust. Dispersed lead is detected by EDX throughout the dark paint layers where it is not associated with distinct lead-containing pigment particles. The amount of lead is considered too excessive to be from an added drier (see also Chapter 3). DTMS analysis of isolated samples of the dark paint identifies large amounts of fatty acid components and lead as well as some lead azelate indicating the presence of lead soaps. The lead soaps may result from dissolution of lead white from the same layer or an underlying layer, in this case the priming layer. The dark paint is very medium rich providing a possible source of free fatty acids that can react with the lead white. It is notable that the lead white in the second ground layer appears severely saponified in all the cross-sections examined (Fig. 4.6.10). Nearly all the original highly scattering particulate lead white pigment has reacted away and transformed into lead soaps, as can

\(^{29}\) XRD analysis was also tried on an isolated sample of the crust, but, unfortunately, this measurement didn’t turn out to be successful: there were only some weak broad bands visible in the spectrum after two hours measuring; it was not enough material for XRD and/or the crust components are too amorphous. With thanks to Keet Goubitz, University of Amsterdam, Department of Crystallography, April 2007.
White hazes and surface crusts on dark oil paints

Fig. 4.6.1 Rembrandt van Rijn, *Homer*, (Mauritshuis, inv. no. 584), 1663, oil on canvas (lined).

Fig. 4.6.2 Crust formation on black area of drapery of lower edge.
be seen by the less dense (grayer), amorphous character of the layer in the backscatter images (see also Chapter 5). Mass peaks at \( m/z \) 348-350, characteristic of lead azelate soaps, were also detected by DTMS in a separate isolated sample of the ground (MH 584x18), which gives further evidence of the presence of lead soaps. The horizontal and vertical gradients of finely dispersed lead (soap) particles, as shown for example, in the backscatter images of a cross-section from the hand (MH 584x35) (Fig. 4.6.9), suggest diffusion from the saponified underlying layer through the paint layer towards the surface.

It is inferred that most of the potassium present in the crusts comes from the smalt, a blue cobalt-containing potash glass\(^{30}\), that was generously used in the dark paint mixtures in the *Homer*. In all the cross-sections studied, the smalt particles are almost completely discolored. Semi-quantitative EDX measurements of the smalt particles reveal very low levels of potassium (less than 1 wt%). Instead, high levels of potassium were detected in the matrix between the pigment particles, and at the surface of all the cross-sections, indicating that the potassium is depleted from the smalt particles and has migrated to the surface, probably as soaps. Cobalt, used to color the glass, is detected at 3-4 wt% demonstrating that a rather pale variety of smalt was used [compare results with Spring et al. 2006]. The low concentrations of arsenic, nickel, iron and bismuth in the smalt are impurities of the cobalt ore.\(^{31}\) The EDX maps for silicon, potassium and cobalt clearly illustrate the leaching of potassium from the pigment particles. The silicon map helps to locate the smalt particles. The cobalt-rich areas correspond to the smalt particles, but the map for potassium registers this element only in the matrix between the particles and at the surface. As shown above in the FTIR spectrum of the surface crust, potassium is partially present in the form of potassium soaps. Our observation are in accordance with recent studies on the degradation of smalt in oil, where it is shown that during the discoloration process potassium is leached from the glass, and reacts with fatty acids from the oil medium forming potassium soaps that subsequently migrate to the surface [Boon et al. 2001; Spring et al. 2005]. Like lead soaps, these potassium soaps are very mobile. Spring et al. identified potassium soaps, as well as calcium oxalates in some cases, in the surface crusts using FTIR. Although expected to be more common, sulfates were not identified/mentioned on the deteriorated smalt films. However, in smalt reconstructions carried out by the same researchers at the National Gallery London, potassium sulfates were also detected other than potassium soaps [Spring et al. 2005]. The source of sulfur/sulfate in these test films must be from the atmosphere. Salts of calcium and potassium, among which potassium sulfates such as arcanite \((\text{K}_2\text{SO}_4)\), have been reported to be present as deterioration products on potash-lime-silica glass [Woisetschlager et al. 2000].

The SEM data demonstrate that smalt particles have also provided direct reaction sites for the formation of the lead-potassium degradation products. This was

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\(^{30}\) Potassium was added in ancient glass to decrease the melting point.

\(^{31}\) According to Muhlerhaler and Thissen, the principle cobalt ores used in the manufacture of smalt in the 17th century were smaltite \((\text{Co,Ni})\text{As}_3\)), erythrite \((\text{Co,Ni})_3\text{[AsO}_4]_2\cdot\text{H}_2\text{O})\) and cobaltite \((\text{Co,Fe})\text{AsS}) [Muhlerhaler and Thissen 1993: 113-115]. See also Riederer [Riederer 1968].
shown for instance in the SEM backscatter image and EDX maps of a cross-section of the cap (MH 584x06). Lead, potassium and sulfur were detected in the rims of large smalt particles. These accumulations of very fine powdery, highly scattering material around the smalt particles have a similar morphology to that observed in the surface crust.

Apart from smalt, the substrate/mordant of organic lake pigments may also be a source of potassium. Lake pigments were prepared by the precipitation or adsorption of an organic dyestuff onto an insoluble inorganic substrate, usually hydrated aluminum by the addition of alum (a potassium-aluminum sulfate) and alkali, possibly with some modifications like calcium carbonate [Saunders and Kirby 1994]. Frequently, some sulfur and potassium are detected by EDX in the lake substrate other than aluminum that is likely to be residual alum or potassium sulfate, material left over from the lake making process that was not completely washed away [Kirby et al. 2005]. That the substrate can adsorb lead and act as direct reaction side for the formation of a lead-potassium-sulfate deterioration product is seen in the backscatter images of a cross-section from the dark garment of the Homer, where some of the aluminum-substrated red lake particles present in the intermediate paint layer are noted to have lead-rich rims.\(^{32}\) We also measured higher intensities of potassium and lower intensities of aluminum at the rim compared to the center/middle/core of the lake particles suggesting decomposition of the lake substrate/diffusion of the potassium component.

Thus, it is thought/postulated that the crusts arise from the migration of lead and potassium towards the surface, possibly in the form of soaps, where they react with carbon dioxide and sulfur compounds from the atmosphere to form insoluble complex salt mixtures. With time, sulfates would be expected to predominate, since these are the most thermodynamically stable species [Woisetschläger et al. 2000]. The insoluble character of these crusts is related to the presence of lead, since potassium soaps and potassium sulfates alone are water-soluble. It appears that the mobile lead soaps trap the potassium compounds and vice versa, or that the lead and potassium soaps easily fuse into each other and then undergo further reactions. The presence of calcium oxalates in these crusts certainly adds to their insoluble character.

The source for calcium is less straightforward; it may derive from the smalt, (yellow) lake or bone black. Calcium can be leached from the smalt in the same way as potassium, but slower. Indeed low concentrations of this element were detected in the paint matrix between the smalt particles. Calcium-rich crusts have been identified on the surfaces of glass objects. In the glass literature, though, the calcium is assumed to originate mainly from the atmosphere [Lefèvre et al. 2002]. The occurrence of calcium oxalate crusts/films is often being associated with the intervention of micro-organisms. Laboratory tests, though, have shown that oxalates may also derive from oxidative degradation of organic materials [Cariati et al. 2000]. This may well be the case here.

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\(^{32}\) A similar phenomenon relating to the presence of red lake and lead was recently observed in the underpaint of the cap of Rembrandt (Studio), *Man with Red Cap* (Rotterdam, Boymans van Beuningen Museum) [Van Loon and Keune 2007a].

157
Fig. 4.6.3 Cross-section MH 586x04 from a black brushstroke in the garment (upper left), FTIR spectrum surface crust (upper right) and FTIR images (lower left and right).

Fig. 4.6.4 EDX spectrum of white crust.
White hazes and surface crusts on dark oil paints

Fig. 4.6.5 Cross-section in UV fluorescence (upper left), SEM backscatter image (upper right) with EDX mappings (lower left and right).

Fig. 4.6.6 FTIR transmission spectrum of white crust.
Chapter 4

Fig. 4.6.7 SEM backscatter detail of cross-section (MH 584x56) taken from the left sleeve showing high scattering crust at the surface.

Fig. 4.6.8 SEM backscatter image showing the embedding of a Si-Al particle in the crust.
White hazes and surface crusts on dark oil paints

Fig. 4.6.9  SEM backscatter image showing horizontal and vertical gradients of finely dispersed lead (soap) particles.

Fig. 4.6.10  SEM backscatter image showing severe saponification of the upper second ground (MH 584x05).
It can be concluded that the formation of a whitish surface crust that drastically alters the tonality of the painting is the result of migration of components in the paint to the surface where they interact with the atmosphere and form new stable mineral phases. The critical factors involved in the severe degradation of the dark areas predominantly lies with the presence/saponification of lead white in the upper ground layer, as well as the composition of the dark paint layers containing smalt that was found mixed with small amounts of bone black, lakes and earth pigments. Here the large amount of smalt was expressly used in order to give texture and bulk and translucency to the paint, rather than to provide color. This reflects the ‘rough manner’, so characteristic of Rembrandt’s late style that is typified by his predilection for broad brushstrokes and thick, translucent paint mixtures. It is considered that the extreme environmental conditions, previous restoration treatment and even display conditions (exposure to direct sunlight) have accelerated/exacerbated the degradation process. Both the saponification of lead white, and depletion of potassium from the smalt are promoted by high relative humidity and temperature. It is very likely that migration processes have been facilitated by the heat exposure from the fire\textsuperscript{33}, as well as that possibly incurred from past lining/s. It is notable that dark areas in *Aristotle with a Bust of Homer* (New York, Metropolitan Museum of Art), painted 10 years earlier in 1653, also exhibit crust formation.\textsuperscript{34} A whitening effect associated with possible crust formation has also been observed in dark areas in other late Rembrandt paintings, such as the *Trip* portraits, dating from about 1661 (London, National Gallery), and Rembrandt’s *Lucretia*, 1663 (Washington, National Gallery of Art). These paintings show similarities in ground structure and in the construction of their dark translucent paint layers, particularly in the extensive use of smalt mixed with red/yellow lake pigments, bone black and earth pigments [Plesters 1980; Bomford et al. 2006; Berrie 1985].\textsuperscript{35} Several cross-sections from the background of *Aristotle with a Bust of Homer*, taken in 1980 by Karin Groen in her study of Rembrandt’s ground layers (held at the Netherlands Institute for Cultural heritage (ICN)), were kindly made available. Re-examination of these cross-sections with SEM-EDX revealed that the lead white in the second, upper ground appears saponified where only the coarse particles are still intact. Furthermore, the pigments: smalt, (alumina-substrated) yellow lake and bone black were identified in the dark paint mixtures.\textsuperscript{36} The identification of the crust has important consequences for conservation practices. Since the crust is not an original part of the paint build-up, it could in theory/33 Consider temperature gradients: the paint surface is warmed up by the heat exposure from the fire, as well as from the lining and direct sunlight from exhibition conditions. We don’t know, however, for how long and how warm. The melting point of lead soaps is 115 °C. Little holes in lead-tin yellow paint from the sleeve give evidence of lead soaps that have melted away. Intact areas shows lead soaps, but in the area with little holes no lead soaps were detected. 34 The Homer and Aristotle have comparable histories; having been commissioned by this Sicilian collector, both were in the Ruffo family palace in Messina during the earthquake of 1783 [Noble et al. 2006]. 35 As observed by Petra Noble during her visits to the Metropolitan Museum in New York and National Gallery of Art, Washington. The reports of the technical examinations of Rembrandt’s *Aristotle contemplating the bust of Homer* (New York) and the *Lucretia* (Washington), carried out by respectively Joyce Plesters in 1980 and Barbara Berrie in 1985/2007 were also generously made available to Petria Noble. 36 The whitening effect as a result of crust formation in the Homer, as well as other late Rembrandt paintings will be taken up in a separate paper ‘White hazes and surface crusts in late Rembrandt paintings’, which is in preparation.
White hazes and surface crusts on dark oil paints

ethically be removed or reduced. The inorganic nature of the crust with the presence of sulfate, carbonate and oxalate species, however, makes it highly insoluble. Furthermore, the SEM studies demonstrated that the crust is so intimately bound to the paint surface, that mechanical removal is also not an option, since it would damage the original paint layer. In the case of The Homer, the final stages of cleaning proceeded under the stereomicroscope, where it was possible to reduce the amount of imbibed varnish in the crust, therefore reducing the degree of whitening. Saturating the crust with a low molecular weight, synthetic varnish, Regalrez 1094 (a hydrocarbon resin), rendered the paint surface more transparent.

‘SIMEON’S SONG OF PRAISE’ (1631) BY REMBRANDT VAN RIJN FROM THE ROYAL PICTURE GALLERY MAURITSHUIS

Simeon’s Song of Praise (inv. nr. 145) is one of Rembrandt’s small-scale history paintings from his early Leiden period (Fig. 4.7.1) [Noble et al. 2006; Noble and Van Loon 2007]. The concentrated shaft of light falling on the central group serves to focus attention on Simeon holding the Christ child, and next to him the kneeling Mary. The scene takes place in a monumental gothic church-like interior. Unfortunately, the spatial depth that is so important in this painting is compromised by a grayish haze in several dark areas in the painting resulting in lost depth and detail. It is particularly disturbing in the large répoussoir curtain of the baldachin in the upper right, where it obscures the original intense dark reddish brown color (Fig. 4.7.1). Blanched gray areas are also evident in the stairs depicted in the right background, and in localized areas of the gray floor in the foreground and near distant left background, appearing as patchy lighter gray areas. The dark reddish brown paint of the chair with the two scribes in the right-hand foreground is also grayed and blanched, though, here it is partly related to optical light scattering from the severely cupped paint layers along the bottom margin (Fig. 4.7.1). The underlying causes that have led to these changes in appearance were investigated, together with the conservator during the recent treatment in the Conservation Studio of the Mauritshuis (2004-2005)³⁸, in order to better understand Rembrandt’s original intention. Samples from the various grayed areas in the painting were taken during treatment and prepared as paint cross-sections to study with light microscopy and SEM-EDX.³⁹

Examination of the surface of the painting under the light microscope (at 100-200x magnification), as well as the surface of an unembedded paint sample

³⁷ The solubility product constants (K_{sp}) at 25 °C are, for example, 2.32x10^{-9} for CaC_{2}O_{4}.H_{2}O, 8.7x10^{-9} for CaCO_{3}, 1.6x10^{-8} for PbSO_{4}, and 5x10^{-14} and PbCO_{3}.
³⁸ Varnish removal was carried out by Jørgen Wadum in 2004; treatment was completed by Petria Noble in 2005, at which time the technical investigation was carried out. The technical examination is taken up in a separate article in Art Matters 4 (Noble and Van Loon 2007).
³⁹ Sample preparation and light microscopy using a Nikon Optiphot-2 microscope were done by Petria Noble in the Mauritshuis Conservation department.

163
Chapter 4

indicates the presence of tiny whitish particles on the surface that are much smaller than the pigment particles themselves (Fig. 4.7.2). It seems logical to conclude that the haze is a result of these white particles. Cross sectional analyses from the dark curtain of the baldachin (MH 145x04) show that the paint layer build up is relatively straightforward, revealing a chalk ground, a cream-colored *imprimatura* consisting of lead white, with additions of chalk, earth particles and fine carbon black, followed by two (or three) almost identical layers of a deep reddish dark brown over the lighter brown sketch layer. The dark brown paint layer contains extremely large rounded particles of carbon-based black pigment as well as (alumina-substrated) red lake and large particles of orangey manganese-poor umber in addition to a little earth pigments, lead white and probably chalk. In addition, the EDX mapping shows an even distribution of lead throughout pointing to the formation/migration of lead soaps. In cross section, this haze appears as a thin grayish crust (about 1 μm thick) at the surface of the top paint layer. It is also visible in the backscattered electron images due to its higher contrast compared to the rest of the paint (Fig. 4.7.2). EDX demonstrates that the whitened surface layer is rich in lead and potassium, as well as a little calcium and sulfur, comparable to Rembrandt’s *Homer*. Unfortunately, the thinness of the deposits in the *Simeon’s Song of Praise* limited further identification/analysis of the deterioration products.

Analyses of the paint cross-sections from the stairs and floor reveal that the paint compositions are similar to that of the curtain. Sample 0145x03 was taken from the stairs at the right edge. Here the paint composition is very similar to that of the curtain, only lighter: red lake, orangey umber, earth pigment, little lead white and chalk (applied in two layers). Sample 0145x01A was taken from the dark gray floor in the lower left background. The floor is built up in two layers: a thick compact grayish brown layer containing charcoal black, lead white (mostly dispersed as lead soaps), earth pigments, as well as possibly a little red lake, followed by a thinner dark gray layer of a similar composition. Again, in both the light microscope and backscattered electron images a (whitish) deposit is visible on the surface that is rich in lead, potassium, calcium, sulfur and phosphorus pointing to similar degradation as seen in the other samples.

Samples from cupped and non-cupped areas from the chair of the scribes (MH 145x05 and 145x06) show that the paint layer build up is relatively straightforward, revealing two layers of dark brown that mostly consists of an organic brown earth pigment, possibly Cologne earth, and a little red earth and dispersed lead on top of the sketch layer. Apart from a high amount of carbon, EDX detected traces of calcium, potassium, aluminum, iron and silicon associated with the brown pigment particles, which is a good indication for the presence of an organic brown earth pigment. We did not try to characterize the brown pigment further with mass spectrometric techniques in this case. In the sample from the cupped paint at the lower right edge (MH 145x05), what appears to be a varnish layer separates the two layers. Very interestingly, in the overlying varnish residues in the sample from the cupped paint, spherical-shaped particles of lead-potassium-sulfur have formed, a whitish compound that was also found on the surface in the other samples from blanched areas, but here crystals have developed (Fig. 4.7.3).
As observed in all cross-sections from grayed dark areas, the severe state of saponification of the lead white particles in the priming layer is remarkable. The dissolution of lead white can be recognized in the backscatter images by their (gray(er) less dense amorphous appearance of the pigment, as compared to the well defined highly scattering intact pigment particles (Fig. 4.7.2).

The causes for the graying of the surface in the various areas of the painting have been shown to be due to the formation of a localized insoluble whitish deposit on the surface of the painting. The degradation products in this deposit, having consistently been shown to contain the elements lead, potassium, sulfur and calcium, are probably a mixture of various compounds such as sulfates, carbonates, carboxylates and oxalates, that are formed depending on the conditions. The results are comparable with whitening problems studied in other (Rembrandt) paintings that also have (bone/carbon-based) black pigment, lakes, smalt and/or earth-containing paint layers that are rich in binding medium and appear to be full of lead soaps (See the Homer case in this chapter, as well as the Wouwerman and Hals paintings). As with the other cases, the lead soaps most likely originate from the underlying lead white-containing priming layer. That the severe state of saponification of the priming layer could be a source of leachable/mobile lead carboxylate components seems to be confirmed by the distribution and amount of lead detected throughout the paint layers. These components are thought to migrate to the surface where they further undergo reactions with other elements from the paint, such as potassium, and the environment including sulfur compounds. As a result, the minuscule insoluble white particles have formed at and near the paint surface, which accounts for the gray haze observed on the painting. The potassium is thought to come from various possible pigment sources, such as the lakes (compare with Rembrandt's Homer) or the earth pigments; smalt, a cobalt-containing potash glass and an important potential source for potassium, is not present in these paint layers. Earth pigments consist of iron and manganese oxides and aluminum-silicates, but usually also contain a certain percentage of calcium and potassium. Potassium occurs naturally bound to other elements in many minerals. Apparently, it can also be leached from the pigment when mixed in oil paint. It is understood that the leachable percentages of potassium in these pigments are much lower compared to smalt. At this stage, it is not clear whether the calcium derives from the paint, or comes from an external source.

It can be concluded that the development of these thin surface deposits/crusts relates to the composition of the paint layers and the presence/saponification of lead white in the upper priming layer. The whitish haze could not be removed during treatment without damaging the original paint, but it could be rendered more transparent by saturating it with a varnish.
Fig. 4.7.1 Rembrandt van Rijn, *Simeon’s Song of Praise*, (Mauritshuis, inv. no. 145), 1631, oil on oak panel. Overall with detail of baldachin (*right*) showing grayish haze.

Fig. 4.7.2 Detail of the paint surface from the baldachin under the light microscope (100x) showing the presence of tiny whitish particles (*left*). The SEM image (MH145x04) reveals a thin surface crust and almost complete saponification of the lead white particles in the priming layer (*right*).
White hazes and surface crusts on dark oil paints

Fig. 4.7.3 SEM backscatter image of cross-section from scribes showing spherical-shaped Pb-K-S particles.

Fig. 4.7.4 Blanched and cupped paint of the chair of the scribes in lower right (macro and microscope detail).
Departure from the Stable (inv. nr. 215) is part of the series of so-called stable interiors of which Wouwerman painted about 50 different compositions during his artistic career (Fig. 4.8.1) [Verhave, Van Loon, Noble 2007].40 A very specific quality of Wouwerman’s stable interiors is the use of dark, almost black backgrounds. He uses them to make his interiors as realistic as possible, with sparse daylight shining in from the stable entrances. Besides making the interior space convincing, the dark colors in the background give extra emphasis to the color accents used in the figures. The blue dresses, red jackets and feathered hats, as well as the white horses depicted in the centre of the painting stand out against the dark background. Unfortunately, the spatial depth is distorted due to whitening of specific areas. Localized whitening along the wood grain has resulted in horizontal grayish stripes (Figs. 4.8.2 and 4.8.3). In addition, in the upper half of the painting, the intended depth of the dark interior of the stable is disturbed by an irregular grayish haze that sits on the upper, dark paint layer. The nature and origin of the whitening were examined together with the conservator during the recent treatment in the Conservation Studio of the Mauritshuis (2004-2005).41 Samples were studied using LM and SEM-EDX.

Surface examination with the stereo-microscope (up to 40x magnification) of the localized whitening reveals that the paint is raised along the wood grain where it seems to have lost its color resulting in a disturbing stripiness. The difference between the whitened areas and intact paint is very distinct (Fig. 4.8.2). Samples from a whitened area and an intact, unaffected area in the dark background at the far right were collected for comparison. Cross-section analyses show that the paint is built up in four layers (Fig. 4.8.3). The panel seems to be prepared with a cream-colored, oil-bound ground consisting of mainly lead white and some earth pigments, followed by an opaque gray imprimatura layer composed of fine lamp black mixed with lead white. Usually, panels were first prepared with a chalk/glue ground before applying a second oil ground or imprimatura, but curiously this chalk layer is absent in all cross-sections. On top of the gray imprimatura layer is a dark paint layer that contains bone black, a little lead white and dispersed lead, some (alum-substrated) red lake, fine particles of red earth and a few copper particles. The copper particles might have been added as drier. Verdigris (copper acetate) was recommended as drier for bone black paints in historical treatises [Van de Graaf 1958]. The dark paint layer is finished with a translucent, warm orangy brown glaze layer (varying thickness 5-15 μm) of which the uppermost part (approx. 5 μm) appears completely colorless in the cross-section from the whitened area, although the shapes of pigment particles are still present. In contrast, the glaze layer in the cross-

40 The pendant painting Arrival at the Stable is also in the collection of the Mauritshuis (inv. no. 214).
41 Treatment and research of Departure from the Stable was carried out by Johanneke Verhave, student of the SRAL, during a 6-month internship in the Mauritshuis in 2004. A separate article on this painting and a pendant painting is appeared in Art Matters 4 [Verhave, Van Loon, Noble 2007].
section from the intact, dark area is not discolored at the surface and demonstrates a uniform warm brown color. Elemental analysis with EDX shows that the glaze layer contains many calcium-rich particles in addition to some larger, now colorless particles with a very high aluminum content, suggesting the presence of substrates for organic lake pigments, yellow or red dyestuffs or possibly a combination of the two. Most red lakes were precipitated on an alumina substrate, whereas the more vulnerable and inferior lakes, such as brazilwood lake and the yellow lakes -known as ‘pinks’ or ‘schiet yellows’ in the 17th century-, were often bound with a high amount of chalk [Saunders and Kirby 1994].

It is striking that these lake pigments have faded selectively along the wood grain, where the paint layers are slightly higher. This whitening phenomenon seems to have occurred because the raised paint has been more prone to friction during cleaning, causing the paint surface to physically break up. This has made the paint layer locally more susceptible to environmental influences.

Yet, another whitening process seems to have taken place in the dark background of the stable. Here an irregular whitish haze, which does not seem to be related to the composition or the wood grain, distorts the blackish paint to such an extent that the spatial depth of the stable is largely lost. This kind of cloudy whitening in dark paint layers is seen in numerous paintings by Wouwerman. Microscopic examination of the surface of Departure from the Stable (at 100-200x magnification) reveals a superficial whitish haze on the paint surface with tiny whitish particles (Fig. 4.8.4), but they could not be visualized in the cross-section prepared of a sample from an affected area. The light microscopic image of a cross section from this area shows that the paint layer build-up is again very straightforward, revealing only one dense paint layer of a warm dark color applied over the dark gray imprimatura and cream-colored ground layer. In addition to a lot of fine particles, this layer contains several larger black and brown particles. SEM-EDX analysis demonstrates that the black particles are a carbon-based black pigment. The other pigments are mostly finely ground earths, and some larger, transparent brown particles are possibly Kassel earth. In addition,

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42 Many of the different pigments used by Wouwerman seem to be affected by this kind of localized blanching along the wood grain. Even inorganic pigments like vermilion and ultramarine seem to be affected by this kind of local whitening/degradation. Vermilion is known to be light-sensitive turning gray/black. This is evidenced in the red jacket of one of the figures in the pendant painting Arrival at the Stable (inv. nr. 214), where gray lines are visible and disturb the modeling of the jacket. The clothing of one of the servants in Arrival at the Stable, painted with a copper green glaze in the shadow areas and with ultramarine in the mid-tones and highlights, has now lost its legibility, because the ultramarine paint has blanched becoming lighter and patchy. Blanching of ultramarine layers, not analyzed in this case, is often found to be caused by physical break-up of the paint matrix, which results in light scattering while the ultramarine particles themselves have retained their blue color.

43 It has also been noted in another stable interior by Wouwerman in the Alte Pinakothek in Munich. Here an ’ungewöhnlichen Störung [unusual disturbance]’ was reported in the background: ’wie eine ‘Milchstraße’ bedecken winzige Pünktchen die Malerei [tiny dots cover the painting like a Milky Way]’. The Munich painting, painted on copper, was reportedly regenerated in 1865, which allowed for the assumption by Schmitt that the ’Milky Way effect’ might be caused by some whitish material having been leached from the ground through the paint layers [Schmitt 1990].

44 Maybe the layer is too thin, or the particles are not concentrated enough in the area sampled, which might make it difficult to expose them in cross-section.
Chapter 4

Fig. 4.8.1 Philips Wouwerman, *Departure from the Stable*, (Mauritshuis, inv. no. 215), 1655-65, oil on oak panel.

Fig. 4.8.2 Localized whitening along the wood grain (detail).
White hazes and surface crusts on dark oil paints

Fig. 4.8.3 Localized whitening along the wood grain due to degradation of a calcium rich surface glaze (layer 4).

Fig. 4.8.4 SEM backscatter image (upper left) and EDX map of lead (upper right) of cross-section from irregular whitish haze showing saponified ground (lower).
this layer includes red and yellow lakes. In cross section, the dark paint does not show any apparent loss in color or the presence of a whitish deposit at the surface that can explain the whitening in the dark background as observed with the naked eye. So, it was not possible in this case to analyze the whitish material. However, the severe state of saponification of the lead white particles in the priming layers, as observed in the backscattered electron images, is remarkable in this cross-section. The gray (less dense) halos around the highly scattering (more dense) well-defined intact particles indicate that the lead white is being transformed into lead soaps (Fig. 4.8.4). Dispersed lead is also detected with EDX throughout the dark paint. This brings us to the tentative explanation of the haziness that some migration or leaching of components from within the paint, triggered by influence of moisture or during past cleaning, has taken place and has deposited on the surface. The severe state of saponification of the ground layer, as demonstrated above, could be a possible source of leachable lead carboxylate components, a hypothesis that seems to be confirmed by the amount of dispersed lead throughout the dark paint layers. There is great resemblance with the previous case study of Rembrandt’s *Simeon's Song of Praise* in build-up of the paint layers and pigment mixtures of the dark paint, with the use of both earth pigments and lakes, as well as in the severe state of saponification of the lead white-containing ground layer. In the dark areas of *Simeon's Song of Praise* it was clearly demonstrated that lead soaps originating from the lead-white containing priming layer had deposited at the surface where they further underwent reactions with other components from the paint and the environment forming a thin insoluble lead-rich crust. Compared to the color and saturation of the paint along the edges of the panels, which were covered by the frame, the freshly painted dark backgrounds must have been warmer, darker and more translucent, suggesting that again environmental conditions must play a part in this degradation as well.

To summarize, the whitening phenomenon has an especially strong visual impact on dark paintings like this stable interior, where even minor changes in the saturation of the almost monochrome dark background are disturbing. Fading of lake pigments and physical degradation of the paint surface along the wood grain, where the paint is slightly raised, have resulted in a localized whitening effect creating horizontal stripes. Furthermore, the irregular haze in the dark background is caused by an uneven deposit of a whitish material on the paint surface, possibly as a result of migration or leaching of paint components from lower in the layer(s).
‘PORTRAIT OF JACOB OLYCAN (1596-1638)’ (1625)
BY FRANS HALS FROM THE ROYAL PICTURE GALLERY
MAURITSHUIS

After varnish removal, oily residues (stains) were left on the surface of the black drapery and gray background in the Portrait of Jacob Olycan by Frans Hals (Fig 4.9.1). It was desirable to characterize these layers to tailor cleaning methods accordingly during the rest of the treatment. Loose sample material was analyzed using DTMS and single-point FTIR transmission. Cross-sections were investigated using light microscopy and SEM-EDX. The residual layers manifest either as blanchy material or as crusty orangey material (Fig 4.9.2). In all/both cases, DTMS analysis of isolated samples from the residues gives evidence of the presence of oil components. The main mass peaks detected are m/z 256 and 284 from the molecular ions of palmitic and stearic acid, and m/z 152 a characteristic fragmentation ion of azelaic acid (C9 diacid). In the higher temperature region, the typical peak pattern of the pyrolysis products of the oil paint network is evident with mainly aromatic components (e.g. m/z 91, 105). The inorganic fraction shows the isotope pattern of lead m/z 206-208, some sulfur m/z 64 and potassium m/z 39, which implies the occurrence of also some mineral components in the residues. Lead and potassium have probably migrated from the underlying paint layers. EDX further confirms the presence of lead, potassium and sulfur, in addition to some calcium, in the higher scattering areas spread over the surface crust as noticed in the backscattering mode (Fig 4.9.1). Additional analysis by single-point FTIR analysis demonstrates high intensities of oil components as well as minor amounts of calcium oxalates and other mineral salts, such as lead carbonate, potassium/lead soaps and possibly sulfates. The presence of calcium oxalates and the other mineral salts partly explain the insoluble character of the oily residues. It was decided to leave the oily residue layers on the surface as a safe method for removal could not be found.

45 Treatment and technical examination of the Portrait of Jacob Olycan was carried out by Alice Tate-Harte, student of the Courtauld Institute in London, during a 6-month internship in the Conservation Studio of the Mauritshuis 2006-2007. The pendant painting Portrait of Aletta Hanemans (Mauritshuis inv. no. 460) was treated at the same time by Sabrina Meloni, but this painting was affected to a much lesser extent, although the paintings have the same treatment records since they entered the Mauritshuis collection.

46 The paint cross-sections were prepared by Alice Tate-Harte in the Mauritshuis Conservation Studio.

47 It may also account for the orangey-brownish color of the residues. Oxalate crusts can vary considerably in appearance, including white, yellow, orange, red, red-brown, brown or black colors [Dorn 2007].

48 Only the most disturbing resinous lumps were be softened with a ethanol/iso-octane gel 1:1 gel, thinned with a scalpel and then rolled over with 1:1 isopropanol/isoctane. It was possible to remove the residues with strong solvent-gels, deoxycholic acid resin soap gel or lipase gels, but this also seemed to affect some of the original paint underneath. See treatment and cleaning record by Alice Tate-Harte, kept in the documentation of the painting at the Mauritshuis Conservation Studio.
Fig. 4.9.1 Frans Hals, *Portrait of Jacob Olycan (1596–1638)*, (Mauritshuis, inv. no. 459), 1625, oil on canvas (lined). SEM backscattered electron image of oily residue on the surface (right).

Fig. 4.9.2 The oil residues manifest either as blanchy material (*left*) or as crusty orangey material (*right*).
White hazes and surface crusts on dark oil paints

Fig. 4.10.1 Unknown artist(s), Painted ceilings with hunting scenes with skies and birds, (Trippenhuis, Amsterdam, corridors and stairwells), 1660-62, oil on panel. Detail showing sample locations.

Fig. 4.10.2 Cross-section images showing the formation of a thin crust at the surface of the lead white smalt paint. Light microscope (upper left), UV fluorescence (upper right), SEM backscatter image (lower left) and detail of crust (lower right).
Chapter 4


The Trippenhuis on the Kloveniersburgwal in Amsterdam was built between 1660-62 by the architect Justus Vingboons for the two brothers, Louys and Hendrick Trip, very wealthy merchants of arms. It is in fact a double house with two residences behind one, shared richly decorated façade and an identical but mirrored floor plan. The original ceilings in the corridors and stairways are decorated with hunting scenes with skies and birds. They were concealed with layers of monochrome overpaint over the course of time, but were re-discovered and re-exposed during the restoration of the Trippenhuis between 1985-92. Unfortunately, the painted decorations are revealed in a rough manner (with paint stripper and mechanically with scalpel knives) resulting in many abraded areas at the paint surface. In addition, the originally blue skies are partly discolored and now appear brownish and patchy (Fig 4.10.1). The ceilings in the southern house (of Louys) were first restored, in the mid-1980s. A few years later in 1992, similar decorations in the northern house (of Hendrick) were revealed. Both have a completely different look now, although originally they must have been similar in appearance. During a recent investigation⁴⁹, samples from the skies of both houses were collected to compare the various paint compositions and relate them to the degree of discoloration as observed on the paint surfaces. Additional samples were taken from both canvas paintings and paintings on wood from the ceilings of the meeting rooms on the first floor, specifically the Bilderdijk Room, the Board Room and the Rembrandt Room, which had not been covered by monochrome overpaint layers and now seem to be in better condition. The sky paints were found particularly relevant in the context of this research on surface crusts, although they are blue and not dark, and they are shortly mentioned here. They contain smalt and lead white and show many similarities in chemical reactivity with other cases discussed in this section, especially with the Homer that also contains huge quantities of smalt. About 15 cross-sections were studied from different sample locations, discolored and intact blue areas, using light microscopy and SEM-EDX.

The various cross-sections from the sky areas demonstrate similar layer structures and paint compositions: a chalk ground, a thin light-gray or light-beige oil-bound ground containing lead white with small additions of earth and/or black pigment, and a sky layer consisting of lead white and smalt. The sky paints reveal comparable particle distributions with partly discolored smalt. A potassium level of 1-2 wt% was measured in discolored smalt particles, whereas the intact blue particles contained 12-15 wt% of potassium. Cobalt was detected at 2.5-4 wt%, demonstrating that a similar grade of smalt was used. The presence of trace elements of arsenic, nickel, iron and bismuth is typical of seventeenth-century smalt. Additionally, the cross-sections show transparent,  

⁴⁹ The Trippenhuis is property of the State Building Agency (Rijksgebouwendienst (Rgd), The Hague). The recent, technical investigation of the painted skies was performed as part of the preliminary research of the painted architectural decoration color schemes of the corridors and stairways in 2006. The ceilings are currently being (re-) restored by Edwin Verweij | Verweij Office for Architectural Paint Research and Conservation Amsterdam and Ruth Jongema | Bureau voor Kleuronderzoek en Restauratie Amsterdam.
White hazes and surface crusts on dark oil paints

brownish areas throughout the layer where the lead white pigment is dissolved and saponified (see also Chapter 5). In the backscattered electron images, these regions appear amorphous and less dense compared to the strongly scattering, intact particulate lead white pigment. EDX measured lower lead and higher carbon concentrations in these saponified areas due to the higher organic content. There seems to be a competition between the formation of potassium and lead soaps. The transparent regions are more abundant in the samples from the discolored, browned sky areas. Therefore, it is inferred that saponification of the lead white pigment is largely responsible for the discolored appearance of the sky paints. Discoloration of the smalt itself appears to play a minor role.

In a few samples where the original paint surface is still intact, because it was protected by layers of overpaint in the past, a thin light gray-brownish transparent crust (up to 5 μm) is visible at the surface of the smalt/lead white-containing paint that exhibits a light-grayish fluorescence (Fig 4.10.2). The crust appears dense (light gray) and amorphous, and is very homogeneous in the backscattered electron images, demonstrating high intensities of lead, potassium and sulfur (Fig 4.10.2). It illustrates once more a diffusion process of lead and potassium, presumably as soaps, towards the surface, where they deposit and form a thin film. The source of sulfur must be from the atmosphere that diffused into the paint. It is thought that this crust formation is not associated with the layers of overpaint that concealed the ceilings, but already started before the ceilings in the corridors and stairways were first covered (probably 50-100 years after their creation). This is borne out of the presence of similar crusts at the surfaces on the sky paints of the ceilings of the meeting rooms, as revealed in the cross-sections. Here, the ceiling paintings have always been exposed and not overpainted.

Discussion

Overview of the different whitening phenomena

In the surface hazes and crusts of the paintings examined here, a whole range of deterioration products were detected, most of them containing lead: lead carboxylates, lead chlorides, lead (potassium) sulfates and presumably lead carbonates. The lead source is an underlying lead white-containing layer. Apart from lead, potassium also appears to play an important role in the formation of such insoluble surface deposits. Potassium soaps and (lead) potassium sulfates were identified. Smalt is an important potential source of potassium, but it was shown that lower percentages of potassium can also be leached/diffuse from other possible pigment sources such as alumina-substrated lake pigments or earth pigments. It seems that the different white products developing in time largely depend on the composition of the dark paints, in addition to external factors. In other cases, the whitish surface layers were found to be degraded calcium carbonate-rich surface layers. Calcium oxalates and lead chlorides were often associated

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50 High concentrations of sulfur vapors may have been present in the atmosphere at the time, owing to stoking coals to heat the rooms in combination with poor ventilation and sewerage.
## Table 4.2 White surface layers: Summary of analytical results

<table>
<thead>
<tr>
<th>Collection</th>
<th>Artist, title, date and support</th>
<th>Sample no.</th>
<th>Paint composition</th>
<th>White product</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oranjezaal</td>
<td>Pieter de Grebber&lt;br&gt;Part of the Triumphal Procession with Spoils of War (No. 24) 1648 canvas</td>
<td>Leather boots highlight HTBS 24x43</td>
<td>3. translucent whitish layer: chalk (earth pigment, bone black, carbon black, lead tin yellow) 2. dark brown paint: bone black, red earth, chalk, umber, lead white (1. ground: lead white, umber)</td>
<td>calcium carbonate</td>
<td>LM FTIR Rama SEM</td>
</tr>
<tr>
<td>Oranjezaal</td>
<td>Pieter de Grebber&lt;br&gt;The Ascension of Frederik Hendrik into Heaven (No. 22) 1649 wooden ceiling</td>
<td>Hair of putti HTBA 22A2</td>
<td>2. dark brown paint: bone black, earth pigment, dispersed lead 1. light-brown paint: lead white (saponified), earth pigment</td>
<td>lead soaps lead sulfate</td>
<td>LM FTIR Rama SEM</td>
</tr>
<tr>
<td>Johan de Witt</td>
<td>Unknown Artist&lt;br&gt;ceiling painting with panel imitation 1652-55 wooden ceiling</td>
<td>Black profile JdWp1.12 D4-Y a, b, c</td>
<td>3. black paint: bone black, umber, dispersed lead 2. gray paint: lead white, carbon black 1. chalk ground</td>
<td>lead soaps (lead sulfate)</td>
<td>LM FTIR Rama SEM FTIRdm DTMS</td>
</tr>
<tr>
<td>Staatliche Museen</td>
<td>Rembrandt van Rijn&lt;br&gt;Portrait of a Standing Man (GK 239) 1639 canvas (lined)</td>
<td>Background GK 293x3</td>
<td>3. dark paint: chalk, red lake, organic brown (Kassel earth?), bone black, red earth, dispersed lead 2. second light gray ground: lead white, lamp black 1. first red ground: red earth</td>
<td>calcium carbonate calcium oxalate lead chloride</td>
<td>LM FTIR Rama SEM FTIRdm DTMS</td>
</tr>
<tr>
<td>Mauritshuis</td>
<td>Rembrandt van Rijn&lt;br&gt;Homer (MH 584) 1663 canvas (lined)</td>
<td>Dark garment lower edge, centre black brushstroke MH 584d04, s19</td>
<td>6. black paint: bone black (smalt) 5. brown paint: smalt, bone black, yellow lake, red earth, dispersed lead 4. intermediate varnish 3. translucent dark brown sketch: Kassel earth, red earth, silicates, lakes 2. second ground: lead white (saponified), chalk, earth pigment (umber), black 1. first ground: chalk, earth pigment (umber)</td>
<td>Lead-potassium-sulfate calcium oxalate</td>
<td>LM FTIR Rama SEM FTIRdm DTMS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Black line in cap MH 584d05</td>
<td>2. black paint: bone black, smalt, yellow lake, red earth, dispersed lead 1. second ground: lead white (saponified), chalk, earth pigment, black</td>
<td>idem</td>
<td>LM FTIR Rama SEM</td>
</tr>
<tr>
<td>Collection</td>
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<td>White product</td>
<td>Analysis</td>
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</tbody>
</table>
| Rembrandt van Rijn | Homer (MH 584) | Cap MH 584x06 | 3. translucent orange paint: smalt, red earth, dispersed lead, bone black  
2. dark brown undermodelling: smalt, bone black, red earth, dispersed lead  
1. second ground: lead white (saponified), chalk, earth pigment, black | idem | LM SEM |
| | | Dark garment lower left MH 584x09 | 5. dark brown paint: smalt, bone black, red earth, dispersed lead  
4. intermediate varnish  
3. reddish brown undermodelling: umber, red earth, bone black, lead white/dispersed lead, yellow lake  
2. second ground: lead white (saponified), chalk, earth pigment, black  
1. first ground: chalk, earth pigment | idem | LM SEM |
| | | Dark garment fire-damaged MH 584x23 | 5. paint  
4. undermodelling  
3. intermediate varnish  
2. black sketch  
1. second ground: lead white (saponified), chalk, earth pigment, black | idem | LM SEM |
| | | Left hand MH 584x35 | 4. thin layer: smalt-rich  
3. reddish paint: red earth, bone black, red lake, organic brown (Kassel earth?), dispersed lead  
2. dark brown undermodelling: bone black, earth pigment, dispersed lead, lake?  
1. second ground: lead white (saponified), chalk, earth pigment, black | idem | LM SEM |
| | | Left sleeve fire-damaged MH 584x51, s30 | 3. translucent orange-brown paint: red lake, organic brown (Kassel earth?), red earth, smalt, bone black, dispersed lead  
2. intermediate varnish  
1. second ground: lead white (saponified), chalk, earth pigment, black | idem | LM SEM DTMS |
| | | Left sleeve Fire-damaged MH 584x56 | 2. paint: smalt, bone black, red earth, lake?, organic brown (Kassel earth?), dispersed lead  
1. second ground: lead white (saponified), chalk, earth pigment, black | idem | LM Raman SEM |
| | | Dark garment lower left MH 584x65 | 6. black paint: bone black, smalt, yellow lake, red earth, dispersed lead  
5. intermediate varnish  
4. reddish undermodelling: red lake, carbon black/organic brown?, red earth, dispersed lead, bone black  
3. black sketch: bone black, red earth, lake?, (smalt)  
2. second ground: lead white (saponified), chalk, earth pigment, black  
1. first ground: chalk, earth pigment | idem | LM SEM |
<table>
<thead>
<tr>
<th>Collection</th>
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<th>Sample no.</th>
<th>Paint composition</th>
<th>White product</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mauritshuis The Hague</td>
<td>Rembrandt van Rijn <em>Simone's Song of Praise (MH 145)</em> 1631 oak panel</td>
<td>Gray floor MH 145x01A</td>
<td>3. charcoal black, lead white, dispersed lead, earth pigment, red lake? 2. imprimatura: lead white, chalk, earth pigment, carbon black (1. ground: chalk)</td>
<td>white product(s) contain(s) lead, potassium, calcium and sulfur</td>
<td>LM SEM</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Stairs MH 145x03</td>
<td>4., 5. carbon black, red lake, umber, red earth, lead white, dispersed lead, chalk? 3. sketch: chalk, carbon black, bone black, umber 2. imprimatura: lead white, chalk, earth pigment, carbon black 1. ground: chalk</td>
<td>idem</td>
<td>LM SEM</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dark curtain, upper right MH 145x04</td>
<td>4. carbon black, red lake, umber, red earth, lead white, dispersed lead, chalk? 3. sketch: chalk, carbon black, bone black, umber 2. imprimatura: lead white (saponified), chalk, earth pigment, carbon black 1. ground: chalk</td>
<td>idem</td>
<td>LM SEM</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Brown chair, lower right corner MH 145x05-06</td>
<td>5. varnish residue with whitish particles 4. organic brown (Kassel earth?), dispersed lead 3. sketch: chalk, carbon black, bone black, umber 2. imprimatura: lead white, chalk, earth pigment, carbon black 1. ground: chalk</td>
<td>Lead-potassium-sulfate (spherical-shaped)</td>
<td>LM SEM</td>
</tr>
<tr>
<td>Mauritshuis The Hague</td>
<td>Philips Wouwerman <em>Departure from the stable (MH 215)</em> 1655-65 oak panel</td>
<td>Beam in stable MH 215x04-05</td>
<td>4. translucent grayish layer: chalk (yellow lake), red lake 3. dark paint: bone black, dispersed lead, red lake, red ochre, copper particles 2. imprimatura (?): lead white, lamp black, red ochre and/or red lake 1. ground: lead white (saponified), earth pigment</td>
<td>calcium carbonate</td>
<td>LM SEM</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dark background MH 215x08</td>
<td>3. dark paint: carbon black, earth pigment, red and yellow lake, dispersed lead 2. imprimatura (?): lead white, lamp black 1. ground: lead white (saponified), earth pigment</td>
<td>not visible or detectable in cross-section</td>
<td>LM SEM</td>
</tr>
<tr>
<td>Mauritshuis The Hague</td>
<td>Frans Hals <em>Portrait of Jacob Olycan (MH 459)</em> (1596-1638) 1625 canvas (lined)</td>
<td>Black drapery and gray background MH 459x4a, a01, a02, a05, a06</td>
<td>2. Successive dark paint layers with carbon black, ivory black, brown earth, lead white and dispersed lead 1. ground: lead white, red lead</td>
<td>oil components calcium oxalate (lead carbonate, lead/potassium soaps, sulfates?)</td>
<td>LM SEM DFTIR dm DTMS</td>
</tr>
<tr>
<td>Trippenhuis Amsterdam</td>
<td>Unknown Artist Painted ceilings in the corridors with hunting scenes with skies and birds 1660-1662 wooden ceiling</td>
<td>Blue sky TKA06 B, L, M, O, R, S</td>
<td>3. sky paint: smalt, lead white 2. imprimatura: lead white 1. ground: chalk</td>
<td>Lead-potassium-sulfate</td>
<td>LM SEM</td>
</tr>
</tbody>
</table>
with these calcareous layers. However, calcium oxalates were also detected in smalt-rich paints and oily residues together with other decay products. This shows how complex the chemical reactions are that takes place in these dark paints, and that usually more than one mechanism is involved. Nevertheless, we can roughly divide the different whitening phenomena encountered on these dark paints into three categories: 1. mineralized lead soaps, 2. mixed lead-potassium-calcium salts and 3. degraded calcium-rich surface layers. The whitish surface deposits in the painted ceilings of the Johan de Witt House and the Oranjezaal by De Grebber were found to largely consist of lead soaps and mineralized lead soaps (lead sulfate). Analyses of the surface deposits in Rembrandt's *Homer* and *Simeon's Song of Praise*, the Hals portrait and the Trippenhuis ceilings show more complex crust compositions compared to the first group. In these paints, also potassium and calcium are involved in the crust formation in addition to lead. In the other paintings examined, the whitening is caused by the degradation of calcium-rich surface layers. This is the case for the whitened shadow areas in the background of the *Portrait of a Standing Man* by Rembrandt, the affected dark boots in the *Triumphal Procession* by De Grebber, the grayed surface of the dark cloak of the old man in De Bray's *Triumphal Procession*, and the wood grain-related whitening in the dark interior of the *Departure from the Stable* by Wouwerman.

**Degraded Glaze Layers**

Cross-section analyses demonstrated the almost exclusive presence of colorless particles of calcium carbonate in the originally translucent glaze layers in the paintings by De Grebber, De Bray and Wouwerman. These translucent surface layers were applied over dark-brown or black underpaint layers to render final modeling, and a rich color and translucent effect. Although this could not be confirmed, the presence of now-degraded organic lake pigments should seriously be considered/should be considered as serious/ most likely option, since calcium carbonate as a filler as a major component to give a translucent surface glaze is rather uncommon at this date. 51, 52 It would have given a rather unattractive light brownish color. As said earlier in this text, organic lakes were usually complexed with alum, but combined calcium salt-alumina substrates are also encountered. The addition of a calcium salt, usually some form of calcium carbonate, to the substrate of the colorant is frequently found in recipes for the more fugitive and thus considered inferior lakes, such as all yellow lakes -known as ‘schier-yellows’ or ‘pinks’ in the seventeenth century and derived from weld, buckthorn berries or sometimes yellow dyewoods (old or young fustics)- and those derived from brazilwood (a red dyewood/51 Personal communication Jo Kirby, senior scientist National Gallery London, 2007. 52 There are hardly published occurrences of such layers where the presence of a faded dyestuff can be ruled out. However, chalk in its own right, not as substrate incorporated in an organic lake pigment, was sometimes added to the paint to give body and translucency, but then in combination with other colored pigments. For example, a substantial amount of chalk mixed with other pigments, particularly earths, to achieve a rich translucent effect was found to be present in the dark-colored glazes to the background of Rembrandt’s *Saskia van Uylenburgh as Flora* [Bomford et al. 2006: 37]. Chalk in oil produces a translucent brown, different from chalk in animal glue which is opaque white (Personal communication, 2004, Leslie Carlyle and Maartje Witlox, HART Project De Mayerne Research Program 2002-2006).
Chapter 4

It is noted that the recipes that have survived from this period typically contain a great deal more chalk than alum, as do the glaze layers in the three paintings analyzed. This was probably for reasons of economy: the redwoods and yellow dyestuffs were the cheaper colorants whereas chalk was cheaper than alum in that time. Likewise, organic dyestuffs precipitated on a mainly chalk substrate have been shown to be less stable compared to those on a pure aluminum substrate [Saunders and Kirby 1994]. In practice most of the calcium carbonate does not take part in the complexation reaction with alum and the dye solution, but merely adsorbs the colorant, resulting in a less stable pigment. The adding of calcium carbonate also moderates the final pigment color. It intensifies the yellow color of the already bright yellow lake pigment, whereas in the case of the red lake it makes a more opaque pinkish red color, but in oil-medium it will still become rather translucent.

Given their large-scale production in the seventeenth century and the many recipes for their preparation, redwood and yellow lakes must have been widely used, despite their very poor permanence of color. However, it is often difficult (or sometimes impossible) to identify their presence in paintings and determine the source of the dyestuff. In many cases, the dyestuff has faded away and it is solely the detection of the residual substrate, a significant proportion of chalk as well as some calcium sulfate and some aluminum hydroxide, that hints at the presence of a now-faded organic lake pigment. Thus, the detection of the larger aluminum-rich particles, together with the calcium/chalk,

53 See for example the Pekstok Papers that describe several extensive recipes for the manufacture of redwoods and ‘schiet-yellows’: recipe to make red lake pigment (from sappanwood): … 90 or 100 Lb. of chalk-white. Stir it thoroughly and put in each tub 50 or 55 Lb. of clean white alum …; recipe to make ‘schiet-yellow’ from 1666: … Then put in 100 Lb. of fine chalk-white with 20-22 Lb. of clean good white alum …; recipe from 1677: … To this is added 140 Lb. finely rasped chalk-white; this is settled with 20 Lb. of clean white groun alum, …. [Hermens and Wallert 1998]. See also De Mayerne recipe no. 32 [Van de Graaf 1958: 49, 151].

54 This was demonstrated in reconstructions of the preparation methods by Hermens and Wallert. Analysis of the substrate using XRD, PLM and SEM-EDX showed the bulk of the material still to consist of calcium carbonate white, with some calcium sulfate and some aluminium hydroxide [Hermens and Wallert 1998: note 5].

55 Personal communication Arie Wallert, curator Rijksmuseum Amsterdam, 2005.

56 In particular, the pinks are difficult to determine, since they are usually highly degraded showing nothing detectable by HPLC. Occasionally, it has been possible to identify the yellow dyestuff when the paint had been protected from light by the frame rebate. In one of the Oranjezaal paintings, the yellow colorant could be successfully identified as weld in a sample from an area of the greenery that had been sheltered from the light by the wooden framework (see also Chapter 2). See also HPLC analyses of green paint mixtures in paintings by Aelbert Cuyp [Spring 2002]. Brazilwood is also very light-sensitive and can fade to nothing visible, a yellowish color sometimes at best, and nothing detectable by HPLC coupled to the array detector. However, HPLC with Fluorescence detection (HPLC-Fluor) can sometimes pick up another – not yet identified – UV absorbing component typical of brazilwood that has no influence on the color of the lake but is more stable than brazilein, the coloring component of brazilwood. Personal communication, 2007. Jo Kirby, senior scientist National Gallery London, and Maarten van Bommel, scientist Netherlands Institute for Cultural Heritage. See also the identification of a degraded redwood lake in a painting by Anthony van Dyck [Schoonhoven 2005].

HPLC-Fluor analysis was carried out on a sample from the degraded glaze on the boots by De Grebber but no dye components could be detected, except for a trace of ellagic acid, i.e. tannin (analysis carried out by M. van Bommel at ICN 2007). The presence of tannin is usually associated with the extraction of red dyestuffs (esp. cochineal and madder) from textile shearings (see also Chapter 2). Maybe a mixture of dyestuffs has been used in this case, including brazilwood. Ellagic acid might also be present in the buckthorn berries (various Rhamnus species) and in yellow dyewoods, in small amounts [Hofenk de Graaff 2004]. Thus, the detection of ellagic acid might give some indication of the presence of a deteriorated dyestuff.
in the Wouwerman glaze point to residual substrate and the presence of a now-faded organic lake. In the surface layers in the De Bray and De Grebber, only trace amounts of aluminum were detected, finely distributed throughout the layer. Maybe in these cases, an excess of calcium salt was added to the dye solution during the manufacture of the organic lake pigment that would not have reacted but be left as extender in the final pigment, or the proportion of alum was just very small.

Calcium carbonate in substantial amounts was also identified in the whitened dark paint of Rembrandt’s *Standing Man* together with some bone black, earth pigment and alumina-substrated red lake. The dark surface layer corresponds to the monochrome underpainting that has deliberately been left visible in the shadow and half-shadow areas of the painting. Here we are inclined to think that large quantities of chalk are used as colorless extender to add body and translucency to the brown sketchy underpaint, and not as substrate of a now deteriorated lake. In the initial dead-color stage Rembrandt not only drew lines but also applied a tone over larger areas using more or less translucent brown, red-brown or gray-brown paints to outline the composition and tonal organization of a painting [Van de Wetering 2000]. The monochrome sketch may have been partly left uncovered to fulfill its tonal function in the painting. These brown paints are usually found to contain bone black and various earth pigments (Kassel earth, umber, red earth), sometimes with small amounts of other pigments suggesting that Rembrandt was using up the remains of paint and mixed them with black or brown pigment [Bomford et al. 2006; Van de Wetering 2000]. Chalk as filler has recently been found in brown sketch layers in *Simeon’s Song of Praise* [Noble and Van Loon 2007], and it was also noted in brown sketch layers in several paintings in the Oranjezaal.57

It seems that several degradation processes play a part in the now whitened appearance of these chalk-rich surface layers. It is not just simple fading of a possible organic dyestuff and the presence of residual substrate that has led to these changes in appearance. It is also noticed in the backscatter images that the paint films appear rather broken up/disrupted and roughened at the surface. So, the process of whitening also seems to involve some physical deterioration of the paint, resulting in an uneven surface and micro-cracks and small voids that scatter light. Moreover, in some cases we were able to detect other degradation products at the surface, such as calcium oxalates and lead chlorides, related to the composition of these paints. This presents a new feature in the complex process of deterioration and altered surface appearance of these translucent calcium-rich surface layers. In addition, at the surface of the glaze layer in the De Bray a very thin, inhomogeneous film rich in lead and arsenic was noticed.

57 See footnote 15.
CALCIUM OXALATES

Calcium oxalate salts could be identified in the affected chalk-containing surface layers in the cross-section from Rembrandt’s Portrait of a Standing Man and in one of the two cross-sections from De Grebber’s Triumphal Procession using FTIR imaging studies. In addition to the strong absorption band of the (calcium) carbonate group at c.1410-30 cm\(^{-1}\) \(v(CO_3^{2-})\), the FTIR spectra show prominent bands at c.1640 cm\(^{-1}\) \(v_a(COO)\) and c.1326 cm\(^{-1}\) \(v(COO)\) that are concentrated at the surface of the paint layer (where the paint appears discolored). These bands are typical of calcium oxalate with the small, sharp peak at c.1320 cm\(^{-1}\) being the most characteristic feature.\(^{58}\) The bending deformation c.780 cm\(^{-1}\) \(\delta(OCO)\) is outside the detection range of the FTIR imaging technique (4000-1000 cm\(^{-1}\)). The high intensity of the calcium oxalate-relating bands at the surface implies a surface degradation mechanism. The presence of calcium oxalate films is commonly encountered on the surface of other calcareous substrates such as marble stone and fresco wall paintings as reflected by the extensive number of publications on this subject, but has thus far gone unreported in calcium-rich oil paint films. However, it is likely that these calcareous substrates are in some way comparable with calcium-carbonate containing oil paint films. Two different degradation mechanisms are put forward in the literature to explain the origin of oxalate crusts that both seem very plausible. They may be associated with the intervention of micro-organisms (biodeterioration) that populate the (paint) surface and can survive due to the presence of organic materials and certain other elements. Oxalates are a by-product of their metabolism: oxalic acid is secreted by the micro-organisms (lichens) and its complexation with calcium ions (from calcium carbonate materials) provides a means for its removal as calcium oxalates, whewellite (monohydrate form) and/or weddellite (dihydrate form). The biogenesis of the oxalate patinas has been ascertained in laboratory tests on marble samples [Monte and Bianchini 2004]. In the second scenario, oxalates are thought to arise from oxidative degradation of organic binders or coatings (oil, proteins, natural resins, organic dyestuffs? etc.) in the surface layers, where oxalic acid is formed, and subsequent reaction of the oxalic acids with calcium ions from calcium carbonate materials. For example, researchers noted a correlation between the organic material and oxalate contents on marble surfaces suggesting the origin of the films from degradation processes of past surface treatment [Rampazzi et al. 2004]. The oxidation of organic material on marble stone specimen was also reproduced in laboratory simulations leading to the formation of calcium oxalate, both whewellite and weddellite, on the marble surfaces [Cariati 2000]. A similar process may also be applicable to calcium-containing oil paint films where we would not necessarily suspect the presence of micro-organisms.

\(^{58}\) Two forms of calcium oxalate are normally found: a monohydrate phase, whewellite, which exhibits absorption bands around 1620, 1320 and 779 cm\(^{-1}\) and a dihydrate, weddellite, with characteristic peaks at 1645, 1350 and 783 cm\(^{-1}\) [Cariati 2000]. We also tried to confirm the presence of oxalates in the surface crusts with Raman spectroscopy applied on the cross-sections. Unfortunately, we could only detect the Raman band at 1089 cm\(^{-1}\) characteristic of the calcium carbonate group.
Oxalate precipitates are also encountered on non-calcareous substrates in artworks such as glass and bronze. On polychrome wood and easel paintings, however, their occurrence has not been noticed till recently [Arbizzani and Casellato 2002; Salvadó et al. 2002; Bracco and Ciappi 2002; Matteini et al. 2002; Sutherland et al. 2005; Spring et al. 2005; Higgitt and White 2005; Sutherland 2006]. These are mostly calcium oxalate salts, but copper oxalates have also been detected on bronze substrates and on paint layers containing copper pigments [Higgitt and White 2005], their identification being based on FTIR and Raman, often in combination with XRD, SEM-EDX (to detect the metal) and GC-MS (to detect the oxalate ion). Very recently, oxalic acids among other oxidation products were detected in several naturally and artificially aged reconstructed oil paints, which were prepared at the National Gallery London, by Keune using GC-MS, showing that their presence is absolutely normal in deteriorated oil paints.\textsuperscript{59} Calcium oxalates were also identified in the surface crust on Rembrandt’s *Homer* among other decay products. Their precipitation is probably associated with the extensive use of smalt in the surface paint layers. It appears that calcium oxalates are more often encountered in deteriorated smalt paints [Spring et al. 2005]. Here, the source of calcium is less straightforward, as compared to the De Grebber and the Standing Man, where calcium oxalates developed on calcium-rich surface layers. However, some calcium is present in the dark translucent paints in the Homer as minor component in the smalt, as part of the yellow lake substrates and as calcium phosphate in bone black. In addition, the first, orangey-colored ground layer contains a lot of chalk. Since the calcium oxalate precipitate is concentrated at the surface, we assume that some diffusion of calcium towards the surface has taken place/is taking place. Thus, the question is in which form the calcium is present when it is mobilized. There is evidence that calcium is leached from the smalt similarly to potassium, though maybe slower. At present, however, it is not entirely clear whether it also migrates to the surface in the form of calcium soaps.\textsuperscript{60} The presence of calcium oxalates in surface crusts on smalt-rich paints is in a way comparable to the formation of oxalate salts on glass objects. A range of simple and complex salts of calcium and potassium, mainly sulfates and carbonates, but also chlorides, nitrates and oxalates depending on the atmospheric conditions have been identified in crusts on the surface of potash-lime-silica glass. In the glass literature, only a minor part of the calcium present in the surface deposits is thought to come from the glass, but the main part is thought to originate from the atmosphere, from the gradual deposition of airborne particles onto the surfaces that are then incorporated in the crust [Lefèvre et al. 2002]. Studies of indoor particulate dirt in museums show the elements silicon and calcium to predominate in the dirt. It must be said that we also detected some larger silica-aluminum containing particles trapped in the crusts on the *Homer* giving evidence of the incorporation of some dirt particles in the surface deposits. Thus, it must be considered that part of the calcium detected in the crusts on the *Homer* also

\textsuperscript{59} This was observed during a research project to study the effect of pigment-medium interactions on the drying of oil paints carried out by K. Keune at the National Gallery London May-September 2006. Publication foreseen. Personal communication Karrien Keune, scientist, 2006.

\textsuperscript{60} From laboratory experiments, we know that calcium soaps are easily formed when grinding calcium carbonate in oil, but it is remarkable that thus far we haven’t found any evidence of the presence of calcium soaps in paint layers.
might have derived from an external source, other than from the paint itself. Sutherland also found evidence of the incorporation of surface dirt in the surface crusts [Sutherland 2005 and 2006].

At the same time we identified calcium oxalates, in addition to some other mineral salts, in oily residues (stains) on the surface of the black drapery and gray background in the Portrait of Jacob Olycan by Frans Hals that were left after varnish removal. The presence of calcium oxalates and the other mineral salts partly explain the insoluble character of the oily residues. They compare to the grayish-brown insoluble crusts on paint surfaces analyzed by Higgitt and White (which often also contained calcium carbonate, sulfate and/or phosphate depending on the environmental conditions) and those analyzed by Sutherland [Higgitt 2005; Sutherland 2005 and 2006].

**LEAD CHLORIDES**
Apart from calcium oxalates, lead chloride-containing deterioration products, possibly cotunnite, are detected at the paint surface of the chalk-rich surface layers in the cross-section from the whitened shadow area of Rembrandt’s Portrait of a Standing Man, and in one of the two cross-sections collected from the whitened dark boots of the Triumphal Procession with Spoils of War by De Grebber. In the cross-section of Rembrandt’s Standing Man, it seems that the lead chloride is formed at the interface with the underlying lead white containing ground. We think that the lead chloride has subsequently diffused to the paint surface. In earlier studies, lead chlorides have been found in lead white-containing oil paints associated with (partially) mineralized lead soap aggregates. X-ray diffraction identified fiedlerite (\(\text{Pb}_3\text{Cl}_4(\text{OH})_2\)) in a protrusion mass from the Anatomy Lesson of Dr Tulp by Rembrandt (Mauritshuis, MH146) [Noble 2002]. SIMS data suggest the presence of lead chloride mineral phases in a large lead soap aggregate, which also contains minium, from one of the Heralds by Christiaan van Couwenbergh in the Oranjezaal [Keune 2005a]. Moreover, lead chloride deposits have been found on three modern paintings, where they were further characterized as cotunnite [Ordonez and Twilley 1997]. They could not be associated with a particular color application. It was assumed that the lead chloride was formed through interaction of a soluble chloride, migrating through the paint layers, with the lead white in the pigment mixture near the surface. Another possibility that was considered is that the lead chloride is in fact phosgenite, a mixed lead chloride-carbonate mineral [Pina et al. 1996], but this wouldn’t correspond to the element ratio \(\text{Pb} : \text{Cl} = 1 : 2\) that was measured by EDX.

**REACTION MODEL FOR FORMATION OF LEAD AND LEAD-POTASSIUM CONTAINING SURFACE CRUSTS ON DARK PAINT LAYERS**
The results presented show that the formation of white hazes and crusts on dark paint surfaces involving the migration of mobile components from the paint that deposit at the surface, not to be confused with degraded original glaze layers, is a gradual and complex process that comprises several steps/stages and depends largely on the
composition of the original paint/initial paint as well as the atmospheric conditions. Metal soap formation and mobilization of metal soaps through the paint layers play a crucial role in many of the crust creations. Their deposition at the surface and interaction with atmospheric gasses and deposited airborne particles eventually leads to insoluble salt compositions. Based on the analytical findings/observations, we propose the following mechanism (see also the schematic diagram in Fig. 4.11):

**Step 1 Formation of metal soaps and other mobile/reactive substances in the underlying paint layers**

Lead carboxylates/soaps are formed as a result of pigment-medium interactions in the paint: lead-containing pigments or driers react with the excess of fatty acids liberated from the oil medium. This reaction is promoted by high relative humidity and temperature. The paintings discussed reveal lead white-rich underlying or priming layers that are an important source of reactive lead (II) cations considering the often remarkably high degree of saponification in these layers as shown by the analytical data. Intact seventeenth-century Dutch stack process lead white has a typical broad particle distribution with coarse and fine particles. In contrast, the saponified lead white layers demonstrate an almost complete conversion/dissolution of the fine particles and gray (saponified) halos surrounding the large particles in the SEM images. The presence of lead carboxylates is supported by FTIR and/or DTMS analyses. At the same time, it is inferred that the medium-rich lead-poor dark paint layers provide/supply the reactive fatty acids to the underlying lead white paints, since these lead white layers alone are usually very medium poor and the dark paint layers themselves lack the presence of coordinating metals. The dark paint layers show similar ingredients: carbon-based or bone black, mixed with earth pigments and sometimes also yellow and red lakes and smalt (in the *Homer*). These pigments are known to be highly oil-absorbing making these dark paints rich in medium. This is supported by the identification of high amounts of oil components in the cases where DTMS of isolated samples from the dark paint layers was possible (in the *Homer* and in the Johan de Witt House ceilings). As the oil paint ages, hydrolysis of the ester bonds of the cross-linked triglyceride moieties takes place producing free saturated monocarboxylic fatty acid groups, dicarboxylic fatty acids and acid-rich network oligomers. These acid groups readily react with metals (such as lead) from pigments and driers to form (double-chain) metal carboxylates [Van den Berg 1999]. It seems that primarily the mono-carboxylics separate from the oil network, that becomes increasingly polar during ageing. The di-carboxylics are less mobile: they are more polar while the monocarboxylics have a more apolar character, and secondly, they have better coordinating properties due to the presence of two reactive acid groups that

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61 The saponification of lead white priming layers seems to be related to the application of dark medium-rich surface paints. In the cross-sections from *Simeoni Song of Praise*, for example, saponification of the lead white-containing imprimatura layer was only noted in the cross-sections from the (whitened) dark areas while in other cross-sections from lighter areas of the painting the imprimatura layer was intact implying the influence of the layer(s) on top.

62 As discussed in Chapter 3, bone blacks as well as other carbonized black pigments take up a considerable amount of oil because of their porous structure and large surface area. This makes black paints highly medium-rich. Therefore, it is quite likely that they have supplied the fatty acids for the lead soap formation in the lower lead white layer that has acted as a sink for the free fatty acids.
Chapter 4

can act as chain builders in the oil network while the monocarboxylics have only one reactive acid group [Van den Berg 2002a; Keune 2005a; Boon et al. 2007].

In paint layers with a potassium source present, there is also evidence of the formation of potassium soaps/carboxylates, that also play a part in the crust formations. These potassium soaps belong to the group of single-chain alkali soaps that are water-soluble in contrast to the metal (lead) soaps. The potassium may be leached from the smalt that is in the process of discoloration (in the *Homer* and the Trippenhuis ceilings) or from other possible pigment sources such as earths and alum-complexed organic lakes (in *Simeon’s Song of Praise*).

Oxidative degradation of the oil paint may also lead to small-chain acid compounds, in particular oxalic acid that preferentially reacts with calcium salts to form calcium oxalates. As said earlier in the text, we also expect some diffusion of calcium (from smalt or another pigment source) towards the surface, possibly in the form of soaps, but this could not be confirmed by the analytical data.

*Step 2 Transport of metal soaps and other mobile substances towards the paint surface*

The paint cross-sections give evidence of a diffusion flow towards the surface of mobile paint constituents, in particular the alkali (potassium) and metal (lead) monocarboxylate soaps that are formed lower down in the paint system. Lead soaps developed in the lead white under- and priming layers were detected dispersed throughout the dark surface layers with higher concentrations of lead at the surface. Potassium soaps or species were detected in the matrix around the smalt particles and in abundance at the surface strongly suggesting that migration takes places.

While the analytical data show clear evidence of the mobility of the carboxylates, the process of migration itself and what drives the migration are not completely understood. It seems that several factors play a role in the diffusion process, temperature and moisture are important driving factors as well as the high porosity/low density and flexibility/low resistance of these dark medium-rich paint films (the matrix), and of course the specific mobility and concentration gradient of the soaps themselves. The process is comparable to the migration of free fatty monocarboxylic acids that are
White hazes and surface crusts on dark oil paints

Fig. 4.11  Schematic diagram showing the dynamics of crust formation.
often being seen deposited on the surface of modern oil (and alkyd) paintings (usually associated to certain color areas) (see introduction). A similar process also must play a role in the formation of the so-called inclusions or protrusions: aggregates of metal soaps that manifest as little translucent-whitish globules/lumps in the paint that may swell and protrude through the paint surface. Their occurrence has been reported in numerous paintings by now and also involves migration/mobility of metal soaps [Noble 2002; Van der Weerd et al. 2002b; Higgitt et al. 2003; Keune 2005a; Boon et al. 2007]. The migration of fats in chocolate, which has been much studied in the food technology, also shows similarities to migration in paint systems [Altimiras et al 2006; Ziegleder various papers]. Fat bloom on chocolate products develops from triglycerides (deriving from the chocolate –cocoa butter and milk fat- or from the filling), which migrate to the surface where they re-crystallize. Very helpful is also the work done by Corkery [Corkery 1998]. He extensively studied the structures and properties (thermotropic mesomorphism and amphiphility /hydrophobicity) of metal soaps and this knowledge can be used to better explain the possible reaction mechanisms involved in the migration processes that take place in paint layers. He proposes that double-chain metal soap molecules (like lead soaps) preferentially arrange themselves in the all-trans, splayed chain conformation (with the hydrocarbon chains extending either side of the metal carboxylate head group). The chains pack together with other chains and the head groups connect with other head groups resulting in monolayers of lead ions between fatty acid bilayers. At raised temperatures, these self-assembled lamellar structures can undergo phase progressions from lamellar crystalline to a liquid crystalline phase where the hydrocarbon chains are in a disordered liquid (or molten) state (the metals remain connected and provide stability) until final disruption and/or eventual decomposition. The flexibility of these so-called liquid crystals provides a lot of potential movement in and between paint layers. Certainly, in the case of treatment that involves heat such as linings or when a painting is exposed to heat during a fire (like in the Homer) lead soaps may be mobilized by this mechanism. However, it is unlikely that saturated lead soaps would undergo a crystalline to liquid crystalline transition at or near room

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63 Several tentative explanations have been proposed for the separation of free fatty acids (also applicable to metal carboxylates) from the oil paint, that only partly describe the process. Williams suggests that physical and chemical incompatibilities caused by film shrinkage, syneresis (the extraction of a liquid from a gel) and changes in polarity from oxidation are responsible for the separation of certain components [Williams 1988]. Van den Berg extends on the phase separation idea suggesting that the less polar mono-carboxylic fatty acids are driven out of the polar oil network [Van de Berg 2002a]. Alternatively, Ordonez and Twilley propose that the migration process is primarily the result of the low glass transition temperature (Tg) of the oil paint film (31-45 ºC) [Ordonez and Twilley 1997]. When the conditions of temperature and humidity are such that the polymerized oil matrix is in the region above its Tg value but the free fatty acids are below their melting point (55 ºC), they can move through the rubbery/viscous oil matrix. Published values of the Tg of aged oil paint films by Whitmore et al. show a marked dependence on type and proportion of pigment as well as moisture content, which may account for certain cases of localized blooming/efflorescence. It is also thought by Koller and Burmester that the free fatty acids form a ‘liquid’ mixture that might move through the paint to the surface and form crystal deposits.

64 The solid fat content of chocolate is of great importance for its stability against migration. Furthermore, the rate of fat migration strongly depends on temperature, because with increasing temperature the liquid fraction of the fat increases and the hardiness and resistance of the chocolate are lost, which both facilitate the migration process.

temperature. It is possible that some mixed metal soaps (with two different metals, e.g., Ca and Co) can form eutectics with much lower transition temperatures. Alternatively, unsaturated fatty acid soaps have much lower melting temperatures and can also drive down the melting temperatures of saturated fatty acid soaps. In the case of normal room temperatures, however, it is more likely that the lead soaps are transported by moisture gradients through the porous dark paint films than by temperature gradients (local differences in temperatures). In this respect, the action of solvents during cleaning or varnishing may also mobilize the lead soaps (better known as leaching). Corkery has put forward a hypothesis for metal soap migration flow as a film transport phenomenon in water. But here the splayed chain theory would be problematic, since the polar sheets running through the head groups are sandwiched by two aliphatic layers that are hydrophobic/water-repellent [Corkery 1996]. However, at the air water interface, a metal soap will form a hairpin conformer (with the hydrocarbon chains at one end of the metal carboxylate head group) in the first layer the polar side being in contact with the water, but successive layers, i.e. Langmuir layers, will be in the splayed chain conformation again. Possibly, the filmic transport could be a very few layers of soaps, possibly 2-5 layers, but possibly more. Moisture transport seems very plausible in these very porous dark paints. In the SEM images of the dark layers, we noticed the presence of nano-cracks in the paint structure at higher magnifications (above 1000x) that may provide transport lines, in addition to the micro-cracks along which flows of lead species are often observed. Maybe the transport of metal carboxylates is also helped by the migration of free fatty acids through the paint. It is also considered that capillary forces play a role in the transport mechanism (similarly to the transport of minerals by water flow that deposit on geological materials, rocks, soil, sediments etc. [Hammerstrom and Smith 2002; Dorn 2007]). Interestingly, the idea of capillary action is now also put forward as transfer mechanism in food products such as chocolate, besides molecular diffusion which has been extensively used to model the phenomenon [Aguilera et al. 2004].

It is remarkable that no protrusion-like aggregates of lead (or potassium) soaps have been formed in the dark paint layers examined, although most of the layers are full of soaps. They rather accumulate at the surface. It seems that the individual lead soaps are particularly easily transported to the surface in these medium-rich and porous layers. In contrast, in compact/dense paint layers with lead-containing pigments, the lead soaps appear to be more easily trapped inside the layer, as shown in the many occurrences of lead soap aggregates in seventeenth-century paints investigated by other researchers, probably because they experience more resistance in their movement towards the surface.

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66 Melting point of lead palmitate and stearate is at approx. 130 °C. In comparison, melting point of the free fatty acids, palmitic and stearic acid, is at approx. 55-60 °C.


68 They propose that chocolate may be microstructurally regarded as a particulate medium formed by an assembly of fat-coated particles. Within this matrix the liquid fraction of cocoa fat (which increases with temperature) is likely to move under capillary forces through interparticle passages and connected pores, possibly showing similarities to the transport of mobile components within a porous paint structure.
Chapter 4

It also must be said that the potassium soaps are considered more mobile than the lead soaps; they act more like normal household soaps. The potassium soap molecules have only one hydrocarbon tail, which makes them smaller and therefore more flexible and also gives them a more amphiphilic character compared to the double-chain lead soaps that are more water-repellent (hydrophobic).

The migration of water-soluble and water-sensitive inorganic salts -such as the potassium sulfates and lead chlorides that were encountered in some of the surface crusts- towards the surface is also thought to proceed by moisture transport. This is further evidenced by the deposition of particles along cracks as seen in for example the cross-section from the *Standing Man*.

**Step 3 Mineralization processes taking place at the surface by interaction with atmospheric gases and particles**

As a result of the migration processes discussed in the previous step, lead and potassium (and possibly also calcium) deposit at the surface of the paint, mostly in the form of soaps. In some cases, the lead soaps precipitate and crystallize at the surface in an energetically favorable orientation (like the lamellar structures as discussed in the previous step). Note that the lead soap crystals in the surface deposit on the Johan de Witt ceiling were lined up as lamellar striations. In other cases, they form new lead compounds (lead sulfates, chlorides and possibly also carbonates\(^\text{69}\)) or complex salts with potassium by interaction with other constituents from the paint layer and/or compounds from the environment. The lead and potassium soaps may react with atmospheric gases that have diffused in the paint film (CO\(_2\), SO\(_2\), or other pollutants like NO, NO\(_2\), etc.) and with atmospheric particles/particulates that deposit on the surface (silicates, alumino-silicates, calcium sulfates and carbonates, carbon, skin, fibres, NaCl, biogenic particles like spores and pollens, etc.) to form new inorganic salts. The activation energies needed for the reactions to take place will be mainly provided in the form of light, which reaches the upper microns of the paint film [Thomson 1986]. The crusts on the *Homer* and *Simeon’s Song of Praise* show fine dense particles of complex salt mixtures. We have also seen the incorporation/embedding of airborne particles like alumino-silicates in the crusts on the *Homer*. The dense, concentric particles noticed in the surface deposit on De Grebber’s painted vault in the Oranjezaal are likely the result of mineralization of lead soaps into lead sulfates, whereas the amorphous areas in this deposit are probably still in the process of mineralization/crystallization.

We have already discussed earlier the origin/source of the chlorides and oxalates in the related sections. They could come either from the paint film or from an external source.

\(^{69}\) Although not identified in large amounts in the crusts examined here, studies of lead soap aggregates in paint layers have shown that the lead soaps mainly mineralize into lead carbonates, probably as a result of subsequent reaction with CO\(_2\) that diffuses into the paint film from the air [Noble 2002; Van der Weerd et al. 2002b; Higgitt et al. 2003; Keune 2005a; see also the lead-tin yellow and red lead paints in Chapter 2]. Therefore, we should also consider the formation of lead carbonates in these lead-containing surface crusts.
Step 4 Continuous cycle
The cycle repeats many times, as hydrolysis of the ester bonds of the oil continues, to reach/produce a crust with a thickness in the order of a couple of microns that is visible to the naked eye. Over time, the crust accumulates and changes in composition becoming increasingly insoluble. The soluble crust components (esp. the potassium species) dissolve and remineralize/recrystallize in response to fluctuations in humidity and/or pH conditions to form new, more stable mineral phases. It is also thought that the exposure to organic solvents during cleaning or varnish application may alter the composition of the crust and influence the crystal morphologies, since the organic solvents will extract or dissolve the more soluble crust components. Certainly, the presence of lead compounds and calcium oxalates in the surface deposits adds to the insoluble character of these crusts; it seems that the more soluble components are slowly incorporated in the insoluble crust structures.

Consequences for interpretation of analytical data
The presence of dispersed lead in a paint layer not associated with distinct lead-containing pigment particles is often interpreted as indication of the addition of a lead drier [e.g. Groen 1997; Ferreira 2005]. However, the amount of lead in lead-siccattivated oil is usually below the detection limit of SEM-EDX. This was shown in reconstructed paints of vine black in linseed oil with various lead driers added. Therefore, the amounts of dispersed lead detected by EDX throughout the dark paint layers are considered too excessive to be just from a lead treated oil, although some drier is certainly expected to be present, since these dark paints are inherently medium-rich and poor-drying. It is important to show for future data interpretation that dispersed lead detected by EDX throughout the dark paint layers are considered too excessive to be just from a lead treated oil, although some drier is certainly expected to be present, since these dark paints are inherently medium-rich and poor-drying.

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70 The solubility product constants (K_{sp}) at 25 °C are, for example, 2.32x10^{-9} for CaC_{2}O_{4}·H_{2}O, 8.7x10^{-9} for CaCO_{3}, 1.6x10^{-10} for PbSO_{4}, and 5x10^{-14} and PbCO_{3}.

71 The reconstructed paints were prepared by Leslie Carlyle during a MOLART Fellowship in 1999. We embedded samples from the reconstructions and measured them with SEM-EDX, including the following paints: (ZB) vine black (Kremer), freshly pressed linseed oil with no drier; (A-2B) vine black, linseed oil mixed with litharge and decanted, no heat involved; (AH2B) vine black, linseed oil mixed with litharge and heated (150 °C); (ZBAC) vine black, linseed oil, lead acetate powder added during grinding of the pigment in oil (this also caused air bubbles in the paint, see Fig. 3.B.7). Only in the case where extra lead acetate was added during pigment grinding, the lead was detectable by EDX; in the other paints, no lead was detected with EDX, although A-2B and AH2B had certainly accelerated the drying process compared to ZB where no lead drier was added.

72 Carbon and bone blacks are anti-oxidants that retard the drying of the oil. Evidence for the addition of lead driers to these black paints is present in historical treatises, e.g. De Mayerne manuscript [Van de Graaf 1958]. Umber and ochres also have good drying properties, which apart from their warm color might have been another reason why they were added to these dark paint mixtures. Verdigris, a copper acetate, is also recommended as drier in bone black paints by De Mayerne. This might also explain the presence of a small copper-containing particle detected by SEM-EDX in the dark brown paint of the beam in the stable interior by Wouwerman.
lead in these dark paints also may be the result of saponified lead white having migrated (from the same layer or from an underlying layer).\footnote{This is further supported by other observations. One important observation was made by the investigators of the National Gallery in London when they measured a set of test samples in which smalt in oil was painted over a lead white priming \cite{Spring et al. 2005}. The FTIR spectrum of the smalt test paint suggested the presence of other metal carboxylates in addition to potassium soaps, most likely lead soaps, since lead and potassium were detected by EDX in the matrix between the pigment particles in the smalt layer. This is significant since the test film did not initially contain any lead. They concluded that the lead must instead have migrated from the lead white priming, possibly as lead soaps. A second noteworthy observation was made during the investigation by the authors of a Rembrandt (Studio) painting, \textit{Man with Red Cap}, from the collection of the Boymans van Beuningen Museum in Rotterdam \cite{Van Loon and Keune 2007a}. This painting has a so-called quartz ground, which contains negligible amounts of lead. It was found rather unusual that no dispersed lead was detected by SEM-EDX in the smalt paint of the background, since this is commonly encountered in seventeenth-century smalt paints \cite{Groen 1997; Noble and Van Loon 2005; see also Chapter 2}.}

Of course, the migration/movement of free fatty acids and metal soaps between layers also affects the P:S ratios of the individual layers. Furthermore, the particle distribution of saponified lead white-containing layers is altered. These layers are sometimes described as coarse lead white (in a medium-rich matrix), but these are in fact the large residual particles whereas the small particles have reacted away to form lead soaps.

As already noted by Spring et al., the presence of absorption bands at c.1640 cm\(^{-1}\) and 1530-60 cm\(^{-1}\) due to the formation of calcium oxalates in combination with lead and/or potassium soaps may easily be misinterpreted as amide vibrations of proteins \cite{Spring et al. 2005}.

In the case of degraded glazing surface layers containing calcium carbonate, the presence of a now-deteriorated yellow lake or redwood lake should be considered, even though they are difficult to confirm/identify.

**Influence of painting technique**

The paintings discussed show similarities in ground/layer structure and in the construction of their dark paint layers and glazing layers. It is notable that all paintings comprise a lead white-containing underlying layer that is saponified to a higher or lesser degree/extent. We have seen that formation and migration of these lead soaps play an important part in the insoluble crust creations. In addition, the dark-colored layers show similar paint mixtures containing strongly oil-absorbing pigments: carbon-based or bone black in oil, mixed with earth pigments (red earth, umber, Kassel earth) and sometimes also yellow and red lakes and smalt (in the \textit{Homer}). It is thought that the medium-rich dark paint layers are a potential source of mobile reactive fatty acids for the underlying medium-poor lead white-rich layers. Furthermore, their porous structure facilitates the transport of mobile soaps towards the surface. The severe crust formation in the \textit{Homer} is also associated with the extensive/excessive use of smalt in the dark translucent paint.
White hazes and surface crusts on dark oil paints

Likewise, the glaze layers applied on top of the dark paints contain significant amounts of calcium carbonate that were presumably used as substrates of a now-degraded organic colorant. These chalk-based organic lake pigments are particularly vulnerable to (photochemical) degradation.

Therefore, it is thought that the reason for the severe degradation of the dark areas predominantly lies with the composition of the dark-colored paint layers and the organic glaze layers, in combination with the presence/saponification of lead white in the underlying (ground) layers.

**Influence of Environmental and Treatment History**

The whitening processes have taken place in relatively untouched paintings, as well as in paintings that have suffered extreme conditions. Environmental conditions and previous restoration treatments are considered to have exacerbated the degradation processes in several cases. For example, Rembrandt’s *Homer*, commissioned by a Sicilian collector, was in the Ruffo family palace in Messina during the earthquake of 1783 where it is considered to have suffered sustained heat exposure from a probable fire that broke out after the earthquake (no fire is mentioned in the Ruffo archives, but it is recorded as having been rescued). Both the saponification of lead white and leaching of potassium from the smalt are promoted by high relative humidity and elevated temperature. Thus, it is very likely that migration processes have been facilitated by exposure to heat, as well as that possibly incurred from past lining/s (the *Homer* has been lined twice), though direct sunlight from display conditions should also be considered. That there is a direct relationship between the severely degraded light-sensitive organic glazing layers and direct sunlight is apparent in the case of De Groot’s *Triumphal Procession* where its exposure to direct sunlight is known because of its position in the Oranjezaal next to the windows. Furthermore, the painted ceilings in the Johan de Witt House and by De Groot the Oranjezaal are applied directly on the wooden planks of the architectural construction, which may give rise to strong humidity gradients (from outside the room to inside) that promote the formation and migration of lead soaps towards the surface.

It is difficult to assess the extent to which past varnish removal and surface cleaning methods have played a role in the crust formations and their composition, by the extraction and dissolution of leachable paint and crust constituents, or as source of materials, but we can assume they must have a cumulative effect. We should also consider the role of varnish layers in the protection of the paint surface. It seems that

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74 It is notable that the *Aristotle with a Bust of Homer* (New York, Metropolitan Museum of Art), painted 10 years earlier, in 1653, also exhibits crust formation in the dark smalt-rich paints, as well as other late Rembrandt paintings, such as the *Trip* portraits (London, National Gallery), dating from about 1661, and the *Lucretia*, 1664 (Washington, National Gallery of Art) [Plesters 1980; Bomford et al. 2006; Berrie 1985]. The smalt used in such large quantities gives texture and bulk to the translucent paint mixtures rather than providing color. This reflects the ‘rough manner’, so characteristic of Rembrandt’s late style.

75 The historical cleaning methods may have involved the use of soaps, mixtures with abrasives such as ground glass or sand, alkali solutions (soda, ashes in water (potash-potassium hydroxide)), ammonia, urine (contains oxalic acid) etc., which might have introduced new materials in the paint film. Dubois, H., 1996, *A short historical survey of the definition of solvents and their action, in relation with the cleaning of paintings*, Lecture notes 29 March 1996, Limburg Conservation Institute (SRAL, Maastricht).
surface deterioration processes still take place with varnished surfaces, though probably at a slower rate. Certainly, on surface of the Johan de Witt ceiling that is unvarnished and was untouched for centuries, the lead soaps have grown more abundantly, comparable to the surface deposits on many (unvarnished) modern paintings. This illustrates the potential effect of varnishing and the cleaning cycles in the other paintings.

**Implications/Issues for Conservation**

The identification of the surface crusts has important consequences for future treatment. On the one hand, degraded glaze layers applied on top of the black paint layers may turn out to be responsible for the whitened surface appearance. These are an original part of the paint build-up, and therefore we do not want to remove them. On the other hand, however, we may be dealing with surface crusts that arise from migration processes of alkali/metal soaps through the paint layers to the surface and subsequent interaction with the atmosphere to form new mineral phases. Since, in the latter case, they are not an original part of the layer build-up, they could ethically be removed or reduced. The inorganic nature of the crusts with the presence of sulfate, carbonate and oxalate species, however, makes them highly insoluble. Furthermore, the SEM studies demonstrate that the crusts are often intimately bound with the dark paint surfaces that mechanical removal with a scalpel is also not possible since this would damage the original paint layer.

So, if removal is not possible or not an option, how can the appearance be improved? In most cases, the degree of whitening could be reduced by saturating the crust (or degraded glazing layer) with a varnish. The varnish penetrates in the paint structure, and fills up the voids and micro-cracks and coats the particles. This lowers the amount of light scattering and renders the crust (or degraded surface glaze) more transparent. In particular, a low molecular weight (low viscosity) resin like Regalrez 1094 (a synthetic hydrocarbon resin) is used by restorers for this purpose, since it deeply penetrates in the paint structure. In case the whitening is still too disturbing, covering the whitened areas with thin retouches with reversible materials may be considered. It remains arguable, however, how far one would/should go with covering up the original paint surface. Instead, based on the analytical results, we can also make a reconstruction of the original appearance of the paint, either digitally or just in our minds.

We have seen that the metal/alkali soaps are very sensitive to moisture, solvent and temperature gradients. Hence, it is important to realize the effects of conservation treatments that involve moisture, heat and solvents on the mobilization of metal soaps and free fatty acids in and between paint layers to keep them to a minimum. During cleaning and varnish application, the paint is exposed to solvents. It should also be considered that lead soaps are non-swelling in water, but that they readily swell in hydrophobic solvents, which are often used during treatments to wet the paint surface [Corkery 1996]. Lining and consolidation may also involve solvents as well as moisture and heat. To minimize the transport/traffic of mobile paint constituents, it is also essential to control the humidity and temperature in display and storage conditions, as well as the lightning that may further trigger surface deterioration. Certainly more
White hazes and surface crusts on dark oil paints

studies are needed to be able to fully understand the effects of temperature, moisture and solvents on the reactivity of metal soaps and to modify and develop new conservation strategies that minimize the damage.

CONCLUSION

The whitish surface layers may be degraded calcium carbonate-rich glaze layers, probably deteriorated organic lakes, applied on top of the dark paints to create modeling and special color effects. They form an original part of the paint build-up. Frequently, calcium oxalates and lead chlorides are associated with the degradation of these calcareous layers. In other cases, the formation of whitish insoluble surface crusts was found to be the result of migration processes of lead and potassium in the paint, most likely as soaps, to the surface where they interact with the atmosphere to form new stable mineral phases (carboxylates, sulfates, oxalates, carbonates, ...). This sheds new light on the reactivity of these dark paints. The mobilization processes are likely driven by gradients in temperature and moisture, such as direct sunlight in galleries, heat and moisture introduced to linings, or in one case as exposure to warmth from a fire. It is proposed by Corkery that the metal soaps are able to move with water films or readily diffuse as liquid crystals through the paint structures at raised temperatures. It is thought that the reason for the selective degradation of the dark areas primarily lies with the saponification of lead white in the underlying (ground) layer and the composition of the dark paint layers, which contain carbon or bone black mixed with earth pigments, and sometimes red and yellow lakes and large amounts of smalt. It seems that these medium-rich porous dark paints are particularly susceptible to the formation and subsequent transport of metal soaps to the surface. Environmental conditions and possibly past treatment are considered to have exacerbated the deterioration. The crust compositions are not static. Initial crust compositions largely depend on the composition of the paint, while in later stages external factors have a strong influence on the crust compositions. This new information has important consequences for the interpretation and treatment of paintings.

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Chapter 4

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198
White hazes and surface crusts on dark oil paints


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Chapter 4


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