Color changes and chemical reactivity in seventeenth-century oil paintings
van Loon, A.

Citation for published version (APA):

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: http://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
Color Changes and Chemical Reactivity in Seventeenth-Century Oil Paintings
Color Changes and Chemical Reactivity in Seventeenth-Century Oil Paintings

ACADEMISCH PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Universiteit van Amsterdam op gezag van de Rector Magnificus prof. dr. D.C. van den Boom ten overstaan van een door het college voor promoties ingestelde commissie, in het openbaar te verdedigen in de Agnietenkapel op dinsdag 15 januari 2008, te 12.00 uur

door

Annelies van Loon

geboren te Alkmaar
Promotiecommissie

Promotor: Prof. dr. J.J. Boon

Overige commissieleden: Dr. A. Burnstock
Prof. dr. A.G.A. van Grevenstein-Kruse
Dr. J. Kirby Atkinson
Prof. dr. J.P. Filedt Kok
Prof. dr. C.G. de Koster
Prof. dr. P.J. Schoenmakers

Faculteit der Natuurwetenschappen, Wiskunde en Informatica
MOLART Reports

This thesis is the fourteenth in the series of MOLART reports. The MOLART reports summarize research results obtained in the course of the MOLART and De Mayerne research programs supported by the Netherlands Organization for Scientific Research (NWO).

1. Molecular studies of fresh and aged triterpenoid varnishes, Gisela A. van der Doelen, 1999. ISBN 90-801704-3-7


4. Molecular changes in egg tempera paint dosimeters as tools to monitor the museum environment, Oscar F. van den Brink, 2001. ISBN 90-801704-6-1


10. Analysis of diterpenoid resins and polymers in paint media and varnishes; with an attached atlas of mass spectra, Klaas Jan van den Berg (forthcoming).


13. Reporting highlights of the De Mayerne Program, research program on molecular studies in conservation and technical studies in art history, Jaap J. Boon and Ester S.B. Ferreira (editors), 2006.
ISBN 90-77875-14-X


Published MOLART reports can be ordered from Archetype Publications, 6 Fitzroy Square, London W1T 5HJ, UK, Tel: +44 207 380 0800 Fax: +44 207 380 0500, info@archetype.co.uk.

Photo credits
Royal Picture Gallery Mauritshuis, The Hague
Royal Collections, The Hague
Margareta Svensson, Amsterdam
Limburg Conservation Institute (SRAL), Maastricht
State Building Agency (Rgd), The Hague
Edwin Verweij, Amsterdam
Mark Richter, Technical University Munich, Germany
Kröller Müller Museum, Otterlo
Staatliche Museen, Kassel, Germany
# Table of Contents

## Introduction

<table>
<thead>
<tr>
<th>Chapter 1</th>
<th>Improving the Surface Quality of Paint Cross-sections for Analytical Imaging Studies with SR-FTIR and Static-SIMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chapter 2</td>
<td>The Relationship between Preservation and Technique in the Paintings of the Oranjezaal</td>
</tr>
<tr>
<td>Chapter 3</td>
<td>The Whitening of Bone Black in Oil Paint Films</td>
</tr>
<tr>
<td>Chapter 4</td>
<td>White Hazes and Surface Crusts on Dark Oil Paint Films</td>
</tr>
<tr>
<td>Chapter 5</td>
<td>Darkening as a result of Increased Transparency in 17thC Oil Paintings</td>
</tr>
<tr>
<td>Summary / Samenvatting</td>
<td></td>
</tr>
<tr>
<td>Dankwoord</td>
<td></td>
</tr>
<tr>
<td>About the Author</td>
<td></td>
</tr>
</tbody>
</table>
COLOR CHANGES AND CHEMICAL REACTIVITY IN TRADITIONAL OIL PAINTINGS

Traditional oil paintings are not stable systems, and despite the fact that so many Old Master paintings are considered to be generally well preserved, the oil paint used by the seventeenth-century painters as discussed in this thesis is an extremely dynamic system, much more dynamic than is usually thought. Paintings are, in fact, subject to all kinds of chemical and physical processes taking place on a micro and molecular level in the paint layers that only over time (eventually) become visible changing the original appearance of the work of art. These processes are inherent to the artist’s choice of materials and his working methods. They are triggered or accelerated by external factors, such as light, moisture, heat, atmospheric pollutants, from display, storage or certain conservation and restoration interventions. Depending on the materials and the sorts of exposure these changes can be extreme or barely perceptible.

Artists’ knowledge of materials can be inferred from historic sources. Seventeenth-century artists were generally well-educated professionals, who were organized in guilds in order to limit competition and to ensure the quality of work. Although they had a thorough knowledge of materials, commercial reasons also played a role in the choice of materials, production processes and speed with which paintings were produced. Artists were usually also well informed about the limited durability of some pigments, their knowledge corresponding with what we know today. Of course, they were not aware of all the possible paint defects that could occur, since some changes have only become visible after 50 or 100 years, or even longer. Historic sources reveal that of pigments and colorants used in traditional oil paintings, the red and yellow organic lake pigments, the blue organic colorant indigo, the blue cobalt-glass smalt, red lead, the blue/green copper pigment verdigris and lamp black were known to be the most problematic when used in oil. The organic pigments are susceptible to light fading, smalt paints have the tendency to turn brown or gray over time, red lead can grow lighter, verdigris glazes often become an opaque brown and lamp black may either darken or become whitish. The reason that they were still used predominantly lies with the limited choice or availability of pigments in that time. In other cases, economical reasons may have prevailed. In the historic recipes, various methods are described to prevent or minimize discoloration, such as limiting a light-sensitive pigment to the underpainting, bleaching the oil medium in the sunlight, substituting another type of binding medium, or the exclusive use of high quality materials [Van Eikema Hommes 2004].

The understanding of the painted work of art on a micro and molecular level has made considerable progression the past ten years partly due to the MOLART (1995-2002) and De Mayerne (2002-2006) NWO research programs, cooperative projects between scientists, conservators and art historians (see MOLART Reports),
but also to the development of analytical instrumentation and growing interest from the museums themselves for this kind of research. This knowledge has important consequences for the art historical interpretation of a painting, as well as for the preservation and presentation of the work of art.

This thesis focuses on changes in appearance in seventeenth-century oil paintings as a result of natural ageing. It involves interdisciplinary research at the boundary of chemistry, conservation and art history. Interpretation problems that arose during restoration treatment of paintings formed the basis for much of the work. The case studies presented include paintings and painted ceilings from the Royal Picture Gallery Mauritshuis, the Oranjezaal ensemble in the Royal Palace Huis ten Bosch, the Johan de Witt house, the Trippenhuis, and the Staatliche Museen Kassel. They were examined in close collaboration with the conservators responsible for their care.

The first chapter addresses the preparation of paint cross-sections and the various analytical techniques, mostly developed during the MOLART and De Mayerne programs for painting studies. Using the techniques as described in Chapter 1, the chemical and physical processes responsible for the degraded appearances of the paintings were investigated. The following four chapters deal with various degradation phenomena as encountered in seventeenth-century oil paintings.

In the case of the unique ensemble of paintings of the Oranjezaal in the Royal Palace Huis ten Bosch, which was extensively investigated as part of this thesis, the paintings have remained in situ under known conditions with minimal intervention since 1650. The ensemble of 40 paintings offered a unique opportunity to investigate changes in appearance and ageing processes and relate them to other known materials and methods used by the various artists, since the external factors are similar. As a result, many new insights in the wide range of degradation phenomena that occur in painting materials of the seventeenth century were possible. Notably most materials are not homogeneous, the differences in quality, depending on the source and manufacture, were found to affect the stability. It was also shown that the composition of the paints, as well as how they were layered influence the reactivity of the paint (Chapter 2).

Lead white, which was extensively used in the ground and paint layers in that time plays an important role with respect to chemical changes. This pigment is very reactive to fatty acid components from the oil medium and has been shown to slowly dissolve under certain circumstances leading to the formation of so-called 'metal soaps' in the paint. These soap molecules are highly mobile and are able to diffuse and migrate through the paint layers. Over the course of the last decade, extensive research has been carried out on the formation of whitish-translucent lumps in the paint that have been revealed to consist of metal soaps [Noble 2002, Van der Weerd et al. 2002, Higgitt et al. 2003, Keune 2005]. These lumps are the result of aggregation of lead (or zinc) soaps: the soap masses grow and expand until they finally break through the paint surface causing paint loss and/or visual disruption of the surface (Figs. 0.1 and 0.2). This thesis will demonstrate that the formation of metal (lead) soaps also plays a prominent role in many other paint defects that degrade the appearance of oil paintings: the conversion of the bone black pigment into a white product (Chapter 3), white hazes and crusts on the
Fig. 0.1 Jan Steen, *Dancing Peasants at an Inn*, c.1646-1648 (Mauritshuis inv. no. 553). Detail of dog showing pinpoint paint loss in the dark areas caused by protruding lead soap aggregates (left). The paint cross-section demonstrates a whitish translucent soap mass formed in the lead white-rich gray underlayer (right).

Fig. 0.2 Schematic diagram representing early, mature and late stages of lead soap aggregate formation in intermediate layer. Stages 1-5: (1) intact paint, (2) early stage showing small aggregates, (3) expansion of the mature aggregate leading to eruption through the surface, (4) protruding aggregate with remineralization, (5) late stage with mature aggregate decapitated after repeated cleaning. See Boon et al. 2002.
Color changes and chemical reactivity in seventeenth-century oil paintings

Chapter 3 describes the whitening phenomenon of the bone black pigment that changes color from black into white. This phenomenon has not been reported before and was observed in seven paintings by different artists in the Oranjezaal. The composition and stability of bone black is also influenced by its manufacturing process, the heating conditions during the charring process of the animal bones, specifically temperature and time of exposure, that largely determine the quality of the pigment. In other cases, the whitening of the black paints is caused by the formation of insoluble white hazes and crusts on the paint surface, which is the topic of chapter 4. This chapter also includes examples from other museum collections and historic interiors. It shows the complex chemistry of these dark organic-rich paint films, which involves dissolution and migration of paint components to the surface, in particular alkali and metal soaps.

The darkening of oil paint films as a result of increased transparency is the subject of the last chapter. This disturbing phenomenon has been observed and noted for a long time in paintings. New research shows that metal soap formation plays an important role in the darkening process.

**How do we recognize these changes?**

The recognition of degradation phenomena and color changes on (the surface of) the painting and their subsequent identification in paint cross-sections has been the starting point of this study. The painting itself was used as an important source of information.

**Macroscopically**

Some color changes are easily recognizable with the naked eye since they do not correspond with the iconographical meaning of the painting. For example, leaves that now appear blue, because of loss of the yellow component (Fig. 0.3), or brown, due to pigment-medium interaction (Fig. 0.4); or the dark hair of a young man that has (partly) turned white due to chemical conversion of the black pigment into a white product (Fig. 2.11). In many cases, the deterioration is very subtle and can be difficult to notice/assess. The increased transparency of the oil paint, for example, usually only becomes apparent in extreme cases, when a dark underdrawing, underpainting or part of an earlier composition becomes disturbingly visible through the overlying paint that has become increasingly transparent over time (Figs. Chapter 5). Many of these changes in appearance have not been recognized until recently, such as the now uniform brown (originally green) ceilings in one of the rooms of the Johan de Witt house in The Hague (Fig. 0.5). It is only after paint analyses, that it makes sense that this room corresponds to what was called the ‘green’ room in the historic documents describing the history of the house (there was also the ‘red’ room with a ceiling decorated in red tones). Many deterioration phenomena have been misinterpreted in the past, such as the now widely recognized transparent lumps in lead-tin yellow paints (Fig. 2.12-13), which was once ascribed to an emulsion paint. Here the lumps were interpreted as proteinaceous
inclusions [Kockaert 1973/74]. The research of metal soap aggregation, however, has demonstrated that these lumps (and resultant craters) are caused by soap masses formed as a result of interaction of the pigment with reactive components from the oil medium. Changes in color, unusual patchiness or spottiness, severe cracking or changes in texture or gloss may also help in recognizing paint defects and alterations on the paint surface. In this regard, careful surface examination with the stereo-microscope (10-40 x magnification) is instrumental. Indications may also be gleaned by checking the margins of the pictures, the part usually covered by the frame where the original color may be preserved (Fig. 2.4). Delving underneath later overpainting, or inside a broken piece of impasto provides evidence to the painting’s original appearance. Contemporary documents, prints, drawings made after the painting may be helpful in constructing the original colors and composition, such as for example the written document concerning the Johan de Witt house mentioned above [see also Noble and Van Loon 2007: 29, 32; Spring et al. 2001].

**Mikroskopisch**

When close examination provides strong indication that the paint is discolored, this can be further investigated by taking a minuscule paint sample and embedding it in a block of resin that is subsequently cross-sectioned and polished to reveal the stratigraphy of the paint. It may be necessary to first examine a sample from an intact area in order to make comparison with the area suspected of having degraded. By examining the paint cross-section at high magnification (200-500x) with the light microscope, the visual characteristics of the various layers and pigment particles are revealed, such as color, shape, size and distribution. Alterations of the paint are often visually distinguishable from intact paint by differences in color, transparency, fluorescence or particle morphology. Often a gradient is visible in the paint in cross-section, for instance in the case of organic lake pigments (Fig. 0.6) and vermilion (Fig. 2.31), only the upper part of the layer is discolored under the influence of light, whereas the underlying paint is still intact. As to the formation of hazes and crusts on dark paints, a white surface deposit may be detectable in cross-section (Figs. Chapter 4). In other cases, it is the individual pigment particles that have changed in color, for example bone black particles that have turned white (see Chapter 3), or blue-gray smalt particles that are now translucent (Fig. 0.7). In some cases, the color of the pigment particles themselves has stayed intact, but rather it is the paint medium/matrix surrounding the particles that has darkened or has physically become broken up resulting in increased light scattering and lightening of the paint (Fig. 0.8). Cross-sections of transparent regions of paint as a result of saponified lead white particles often show an absence of distinct particles, the increase in organic matter giving the impression of a more medium-rich layer compared to unaffected layers. Such layers are also thicker since the soaps take up a larger volume than the intact pigment and have been shown to lead to delamination of the surface paint (Fig. 5.8). Cross-sections with metal soap aggregates demonstrate large globular, whitish translucent masses in the paint that often protrude through the paint surface (Fig. 0.1).
The surrounding paint is often deformed owing to expansion of the masses. The lead soap aggregates usually exhibit strong UV fluorescence.

Chemically
The paint compositions and deterioration processes can be further characterized on a micro and molecular level using advanced chemical analytical methods, such as scanning electron microscopy, infrared and Raman spectroscopy, mass spectrometry, chromatography and X-ray analyses. The chemical imaging of paint cross-sections was developed during the MOLART and De Mayerne programs (1995-2006). Chapter 1 further explores the preparation of paint cross-sections and analytical cross-sectional imaging with specular reflection FTIR and secondary ion mass spectrometry (SIMS). The highly surface-sensitive analytical imaging techniques require high standards for sample preparation. A systematic dry polishing method was developed that resulted in higher quality of the analytical data.

As will be shown in this thesis, the combined use of scanning electron microscopy (SEM) with specular reflection Fourier transform infrared (SR-FTIR) imaging or Raman microscopy proved to be very effective in directly characterizing the original paint components and alteration products in cross-section. EDX coupled to the electron microscope was used for elemental analysis. The mapping facility reveals the distribution of the various elements in the cross-section, the map overlays aiding in the identification of compounds.

In particular, the cross-sectional images obtained with the scanning electron microscope (SEM), the so-called backscattered electron images, give significant insights in the chemical changes of the paint layers. These high resolution images show the dissolution of pigments or the formation of new products, as well as migration flows of mobile paint constituents within and between paint layers. Since backscattered electron images are contrast images, they illustrate the distribution between the heavy and light elements in the sample and thus provide compositional information about the layers. In addition, since they reveal the particle shape and morphology of the pigments, therefore any degradation products formed will be made visible. Generally a different morphology is a good indication of whether a compound is formed in the paint as a result of degradation, or is a constituent of the original paint. The SEM images in Fig. 0.9 show the amorphous appearance of a number of lead-containing degradation products in the paint. In contrast, intact Dutch stack processed lead white has a much more distinct particle definition. Lead is a heavy element and therefore the lead-containing compounds are strongly scattering and appear white or gray in the SEM images, depending on the density, in contrast with the dark appearance of the organic matrix. Specular reflection FTIR and Raman techniques provide structural information of the various compounds present in the paint. They identify IR active functional groups

---

1 Until recent times, lead white was made by the so-called Dutch stack process. Strips or ‘buckles’ of metallic lead were placed in porous earthenware pots over weak acetic acid (vinegar), stacked in tiers in sheds with fermenting (horse) manure that produces heat and CO₂. The combined action of acetic vapors, CO₂ and heat slowly transformed the lead to white basic lead carbonate [Gettens et al. 1993].
characteristic of organic materials like binding media (e.g. hydrocarbon C-H, carbonyl C=O, hydroxyl O-H, amide -CONH-), as well as inorganic materials, such as pigments and their alteration products (e.g. metal carboxylates/soaps (COO$^{-}$), carbonates (CO$_3^{2-}$), sulfates (SO$_4^{2-}$), phosphates (PO$_4^{3-}$), oxalates (COO$^{-}$), silicates (SiO$_3^{2-}$). Hence, in combination with elemental analysis by EDX many of the deterioration paints to be discussed in this thesis could be identified in cross-section. In some cases, additional analysis was performed on isolated samples to characterize the binding medium, organic dyestuff or crystal structure using direct temperature resolved mass spectrometry.

Fig. 0.9 SEM backscattered electron images of paint cross-sections showing various manifestations of lead-containing degradation products in the paint: deposition of lead chloride (upper left), deposition along crack (upper right), dissolution of lead white particles that show grayer peripheries (middle left), deposition of lead soap crystals at the surface (middle right), lead soap aggregates in lead-tin yellow showing mineralization bands (lower left), deposition of lead-potassium-sulfates at the surface (lower right).
Color changes and chemical reactivity in seventeenth-century oil paintings

(DTMS), high performance liquid chromatography (HPLC) and X-ray powder
diffraction (XRD) respectively.

On the basis of analytical results, the underlying causes that are responsible for the
observed changes in appearance will be further discussed in this thesis. In general,
the paint samples provide a good understanding of the various chemical and physical
processes that take place in traditional oil paints, and they show the inhomogeneity and
complexity of the paint. The paints are in the process of deterioration. It is expected that
the processes will continue and will eventually destabilize the paint. It is hoped that this
research will form a good basis for further model studies, to simulate the deterioration
processes under known conditions and to investigate the influence of the individual
external factors on the reaction rates. These kinds of future studies are necessary to
evaluate storage/environmental conditions and the impact of restoration treatments to
better preserve the artwork for the future. Additionally, by means of the identification
of the present paint composition, it is often possible to deduce the original composition
or intention. Therefore, the information provided in this thesis should also be useful in
reconstructing the original appearance of the painting, either mentally or digitally, which
has direct relevance for the art historical interpretation as well as the treatment and re-
presentation of the artwork in a museum. The implications for conservation will also be
discussed in this thesis in conjunction with the deterioration phenomena in the relevant
chapters.

Publication List

This thesis is based on the following publications:

Chapter 1

- Annelies van Loon and Jaap Boon, 2004, ‘Identifying and localizing
  proteinaceous compounds in paint samples using reflection infrared
  spectroscopic techniques’, in Conference proceedings IRUG 6 Sixth Infrared and
  Raman Users Group Meeting, Florence, Il Prato, 29 March – 1 April 2004, ed. M.
  Picollo, pp. 130-136.

- Annelies van Loon, Katrien Keune, Jaap Boon, 2005, ‘Improving the surface
  quality of paint cross-sections for imaging analytical studies with specular
  reflection FTIR and static-SIMS’, in Proceedings of Art’05 Conference on Non-
  destructive Testing and Microanalysis for the Diagnostics and Conservation of the
  Cultural and Environmental Heritage Lecce (Italy) 15-19 May 2005 (CD-ROM),
  unpaginated.
Fig. 0.3 Frans van Mieris, *A Boy Blowing Bubbles*, 1663 (Mauritshuis inv. no. 106). Detail of the painting showing the altered leaves in the vase. They now appear blue instead of green because of loss of the yellow dye component in the paint.

Fig. 0.4 Jan Steen, *Dancing Peasants at an Inn*, c.1646-1648 (Mauritshuis inv. no. 553). Detail of the upper left sky showing the now brown foliage. The green copper-containing paint has discolored as a result of pigment-medium interaction.

Fig. 0.5 Painted ceilings (1652-55) of the Johan de Witt House, The Hague. The panel imitations, originally applied in various green tones, now show uniform brown colors (left). Cross-section analyses revealed a brownish paint containing verdigris (copper green) and lead white that are slowly converting into metal soaps (right).

Fig. 0.6 Paint cross-section showing fading of the light-sensitive red lake pigment in the top layer. See Noble and Van Loon 2005.

Fig. 0.7 Paint cross-section showing discoloration of the blue smalt particles. The large smalt particle at the extreme left is still blue while the smaller particles have turned gray/colorless. See Noble and Van Loon 2005.
Fig. 0.8 Jan Steen, *The Life of Man*, c.1665 (Mauritshuis inv. no. 170). Detail of blue garment of the girl showing grayed/blanched spots in the blue paint (left). Cross-section analyses demonstrated that the ultramarine particles still appear blue, but that the paint matrix surrounding the ultramarine particles is physically broken up, showing micro-cracks at the paint surface that induce light-scattering and lightening (right).

**CHAPTER 2**


**CHAPTER 3**


**CHAPTER 4**


Introduction


• Annelies van Loon, Petria Noble, ‘White hazes and surface crusts in late Rembrandt paintings’. In preparation.

Chapter 5


Other Publications


**References**


Improving the Surface Quality of Paint Cross-sections for Analytical Imaging Studies with SR-FTIR and Static-SIMS

**Abstract** – The importance of high-quality surface preparation for analytical imaging studies of paint cross-sections is illustrated in this chapter. A systematic dry polishing method was developed based on mechanical preparation with the sample fixed in a polishing holder. Using this method, the surface of existing paint cross-sections was re-polished and re-measured resulting in higher quality analytical data. A thin proteinaceous isolation layer in the flesh paint of an eighteenth-century German polychrome sculpture by Ignaz Günther was studied using specular reflection Fourier transform infrared (SR-FTIR) imaging. SR-FTIR also distinguished the different resinous, proteinaceous and carbohydrate components in the varnish of a Van Gogh painting. In the last example, a cross-section from a painting by Vermeer was examined using static-secondary ion mass spectrometry (static-SIMS) imaging. Here, the higher surface quality led to better mass and spatial resolution.

**Introduction**

Historical paintings and polychromes often show a complex multi-layer build-up with heterogeneous mixtures of organic and inorganic compounds, specifically binding media, pigments and additives. Embedded paint cross-sections are the preferred method of revealing their stratigraphy. The same cross-section can be used for multiple investigations using different non-destructive analytical microscopic imaging techniques. Commonly used imaging techniques are light microscopy (LM) and scanning electron microscopy in combination with energy dispersive X-ray analysis (SEM-EDX). During the MOLART and De Mayerne MOLMAP projects, novel chemical imaging techniques, specular reflection Fourier transform infrared (SR-FTIR) imaging and secondary ion mass spectrometry (SIMS) imaging, used successfully for the analysis of embedded paint cross-sections, in particular the organic components, were developed [Heeren and Boon 1999, Weerd et al. 2002a, Keune and Boon 2004]. SR-FTIR imaging provides information on the distribution of chemical functional groups in a paint cross-section, such as amide groups that are indicative of proteins or the carboxylate group in lead soaps with a spatial resolution of 6 to 7 µm. A full infrared spectrum is collected for each pixel. Results can be displayed as two-dimensional images of a selected functional group to show its intensity distribution on the surface of the cross-section. In a SIMS

---

1 MOLART (1995-2002) brought different disciplines together and created a research platform for the study of the material science aspects of paintings in historical context. It was funded by the Netherlands Organization of Scientific Research (NWO). The De Mayerne program continued this effort for the period 2002-2006. In the MOLMAP project as part of the De Mayerne program, the molecular mapping of paint cross-sections was further explored.
experiment, a primary ion beam rasters over the cross-section surface and generates organic and inorganic secondary ions from the sample, negative ions like fatty acids or positive ions such as lead soaps. Thus, spatially resolved mass information of components present in the paint layer is obtained and can be plotted as two-dimensional images that demonstrate the intensity distribution of a mass peak of interest on the surface of a cross-section with a spatial resolution up to 1 \( \mu \)m. The different imaging techniques are complementary and their combined use provides detailed information on the chemical composition and spatial distribution of both the organic and inorganic substances present in the paint. Knowledge of the composition of individual layers is obtained without the need to separate the layers prior to analysis.

The advanced microscopic techniques, however, require a high surface quality to obtain any results. The surface needs to be exactly in plane and any chemical modification of the layers or smearing of the embedding resin or sample over the surface must be avoided. The polishing step is essential to sample preparation. It is complicated by differences in hardness within the paint, the coarseness of the pigment particles and the overall brittleness of the paint. The existing polishing methods were found to be insufficient and were in need of serious re-evaluation to fulfill the high requirements of surface-sensitive analytical techniques. A recent review of the literature related to making paint cross-sections from easel paintings was written by Khandekar [Khandekar 2003]. Mechanical preparation is the most common method of preparing historic paint samples for microscopic examination. The sample is first embedded in a synthetic resin and ground and polished. Abrasive particles are used in successively finer steps to remove material from the surface until the required result is reached. Microtomning is another method of preparing cross-sections, as well as thin sections. A thin layer is removed from the mounted cross-section with a glass or diamond knife, but the technique is less suitable for the preparation of historic paint samples, since particles or part of the sample easily fall from these brittle paints during the cutting process.\(^2\) However, micromapping is very efficient and successful when preparing more plastic samples from paint reconstructions or from modern paintings. Instead, Van der Weerd developed a double polishing method, where the sample is mounted in potassium bromide (KBr), an infrared transparent medium, for transmission FTIR imaging studies [Van der Weerd 2002b]. Recently, more advanced (and also more costly) preparation techniques are being explored. Ion milling (CP system) [Boon and Asahina 2006] and Dual Beam/Focused Ion Beam (FIB) tools [Lins et al. 2002] were specifically developed for SEM and TEM applications and provide better morphology and particle definition. However, the suitability of these techniques for organic analyses must be examined. These systems use beams of argon or gallium ions for site-specific milling of cross-sections that may damage/destroy organic compounds on the surface.

In this study, we developed a systematic method to dry polish paint cross-sections based on mechanical preparation. This revised method has been successfully applied and has led to significantly better analytical results. For SR-FTIR, the results were improved because the new method increases surface reflectivity. In a static-SIMS

---

\(^2\) Although with care some of the disadvantages can be reduced [Kirby 1977; Derrick et al. 1999].
In this section, different factors that are important for the polishing process of paint cross-sections and the resulting surface finish will be considered.

WET POLISHING VERSUS DRY POLISHING
The abrasion fluid has a cooling role and a flushing role: it prevents the specimen from overheating and removes the loose material. Water, as well as organic solvents such as kerosene, alcohol or oils, are used as abrasion fluids. When paint cross-sections of historic paintings and polychrome are polished, the disadvantages of using abrasion fluid are numerous in our experience. First, soluble paint constituents may be leached out by the abrasion fluid, for example a chalk ground by water or fatty acids by spirit solvents. Second, the blanching of old varnish layers was observed. Third, softer materials erode and hollow out the cross-section. Fourth, weakly bound particles such as coarse minerals may easily be picked up by the abrasive fluid. Fifth, the uneven swelling of the layers during wet polishing causes height differences in the surface. These drawbacks make wet polishing absolutely unsuitable for our purposes. Dry polishing is the only option, and therefore, it is necessary to identify a method that reduces friction and removes loose material.

ABRASIVES
Most commercially available polishing materials are developed for wet polishing. We tested a couple of different brands without the use of an abrasion fluid, but the results were far from satisfactory. Adhesion of the abrasive to its support turned out to be weak and abrasives accumulated on the surface. Diamond paper and powder were also tested by us, but we have to conclude that a diamond abrasive is too hard for paints because it ruins the entire sample. The hardness of silicon carbide (SiC) and aluminum oxide
Improving the surface quality of paint cross-sections for analytical imaging techniques

(Al₂O₃) are similar. Both of the materials can cut glass particles, although SiC is more porous and breaks out more easily causing scratches and pull-outs on the surface. It seems that Micro-Mesh® sheets³, developed for dry polishing of airplane windows, are the only polishing materials with sufficient adhesion and suitability for dry polishing paint cross-sections. The only drawback is that the particle fineness of the sheets does not go below 1 µm, which is not very high in comparison to wet polishing sheets, which can be as small as 0.1 µm, and abrasive powders, such as aluminum hydroxide (Al(OH)₃), which are about 0.04 µm, at their smallest size.

**Polishing Holder**

Our goal is to attain a completely focused image with all the components in the same plane. Any unevenness in level of the cross-section surface will show in reflection imaging. When polishing by hand, the pressure exerted on the cross-section is uncontrolled and often too much resulting in rounded and deformed surfaces and deep scratch grooves. Additionally, excessive weight forces harder particles deeper into the paint layer or particles can be rubbed away from the matrix instead of being cut with the abrasive. Higher forces also increase the temperature at the surface because of higher friction, which may cause thermal damage to occur. Therefore, we use polishing holders that were developed in our institute to exert even and minimal pressure on the cross-section (Fig. 1.1). The cross-section block is mounted with wax or small screws and the height is adjustable to one micrometer. The holder can also rotate on the polishing machine for the first wet steps. The weight of the holder (c. 400 gram) is enough to effect cutting by just moving the holder forward, avoiding extra pressure downwards.

**Mount Dimensions and Shape**

Furthermore, a reduction in the embedding resin surrounding the sample, as well as

---

³ Micro-Mesh sheets are supplied by Micro-Surface Finishing Products Inc., Wilton, Iowa, USA, see their website http://www.micro-surface.com. Micro-Mesh polishing sheets are made of abrasive crystals on a resilient layer over a cloth back. Silicon carbide is used as abrasive for the grades 1500 through 6000; aluminum oxide is used for the finest grades 8000 and 12000.

---
a rounded shape of the resin block, are expected to positively affect polishing results. Polishing by hand makes a larger surface area of the cross-section necessary to keep the resin block oriented as straight as possible during polishing. According to Samuels, mounts smaller than one-inch diameter tend to rock excessively during hand abrasion and polishing operations [Samuels 1982]. A large surface area also increases the risk of smearing out mounting resin on the paint sample or picking up loose particles. When using a holder, the sample is fixed and straight, so that the surface area of the resin can be reduced to a minimum, which is another advantage of the holder.

The shape of the cross-section also affects polishing. A square or rectangular shape provides more resistance at the corners, therefore, a round shape is preferred. The so-called Easy Sections (VWfecit, England) are unsuitable in this respect, because they have a rectangular shape and the length is three times the width, which gives a very uneven resistance.

**TECHNIQUE**

For the preliminary stages, we use a Struers polishing machine with flushing water and coarse silica abrasive paper (grades 500 and 1200) to grind away the mounting medium until almost reaching the sample. Then, we change to dry polishing. After exposing the sample, the sample is left in the holder and the height is not adjusted further for the final polishing steps.

For dry polishing, a very short and straight movement in one direction is made (about 1-2 cm) to avoid as much friction, smearing and heating as possible. No extra downward pressure should be exerted during the movement, only forward. The weight of the polishing holder itself supplies a constant and sufficient pressure to the specimen surface. The polishing holder is turned 90 degrees. Two full rounds are usually enough before going to a successively finer abrasive step (Fig. 1.2). In any case, it is recommended to restrict polishing times to prevent surface modification.

**CONTAMINATIONS**

Loose abrasive particles or other loose particles on the specimen surface can be removed with lens tissue or blown away with nitrogen gas. We have noticed that special lens tissue does not leave scratches on the surface, whereas other papers do. We also recommend using clean polishing sheets as much as the budget allows. Used sheets contaminate the surface when re-used. In addition, they contain many loose particles, which can be picked up by the sample and pressed into the surface of the specimen causing new scratches and pits.

**EXPERIMENTAL**

**SAMPLES**

We selected three representative paint cross-sections to show the importance of surface preparation. These cross-sections were submitted to our laboratory for analysis, but
their surface as received was too poor to obtain satisfactory results. The first sample concerns the flesh paint from the polychrome wooden sculpture of Saint Isidor by Franz Ignaz Günther (c. 1765, St. Francis Xavier altar, Abbey Church in Rott am Inn, South-Germany). The sample is taken from Isidor’s face. Interestingly, it contains a thin intermediate organic layer between superimposed calcium carbonate (chalk) and basic lead carbonate (lead white) layers. This sample was studied using SR-FTIR imaging and additional SEM-EDX analysis was performed. The second cross-section comes from the orangey yellow road in Falling Leaves (Les Alyscamps), painted by Vincent van Gogh in the autumn of 1888 in Arles (Kröller Müller Museum Otterlo inv. no. 224, F486, oil on canvas, 73 x 92 cm). The cross-section shows a thick, yellowed (or better browned) varnish on top of a yellow paint layer consisting of lead chromate, barium sulfate (barite) and calcium sulfate (gypsum) in oil. Isolated sample material of the varnish was analyzed using DTMS and single-point transmission FTIR. FTIR imaging was conducted to localize the different components within the cross-section. The third sample is collected from the background of Johannes Vermeer’s painting Diana and her Companions (c.1655, Mauritshuis The Hague inv.no. 406, oil on canvas, 98 x 105 cm). This paint cross-section demonstrates lead carboxylate aggregates in an intermediate lead-tin yellow layer and primarily smalt particles in the top layer. This sample was examined using static SIMS.4

SAMPLE PREPARATION
The samples were already embedded in either polyester or acrylate resin. Their surface quality was improved by applying the dry polishing method described in the previous section. The sample from Saint Isidor was embedded in Technovit 2000 LC mounting resin, which is a one-component methacrylate that polymerizes under visible blue light (Heraeus Kulzer GmbH, Germany). The Van Gogh sample was embedded in Poly-pol PS230 polyester mounting resin with M.E.K.-peroxide harder (Poly-Service, Amsterdam). The Vermeer sample was embedded in an Easy Section (VWFecit, England) also using Poly-pol PS230 polyester mounting resin.

LIGHT MICROSCOPY
Light microscopic studies of the paint cross-sections were performed on a Leica DMRX analytical microscope (Leica, Wetzlar, Germany). A 100W Halogen projection lamp provided normal reflected light in bright field and in dark field illumination. An Osram HBO 50 high-pressure mercury lamp and Leica filters A (excitation 340-380 nm, emission > 425 nm) and D (excitation 355-425 nm, emission > 470 nm) were used for UV fluorescence microscopy.

SPECULAR REFLECTION FTIR IMAGING
Specular reflection Fourier transform infrared (SR-FTIR) imaging provides detailed information on the distribution of chemical functional groups in a paint cross-section.

---

4 The SIMS measurements were performed by Katrien Keune at the FOM Institute AMOLF.
The FTS Stingray 6000 system was used for SR-FTIR imaging experiments. It combines a Bio-Rad FTS-6000 FTIR spectrometer extended with a Bio-Rad UMA-500 IR microscope (nowadays Varian, Inc., Palo Alto, California, USA) and a MCT detector (4000-1000 cm\(^{-1}\) range), which is a 64 x 64 pixels MCT Focal Plan Array system (Santa Barbara Focal Plane, California, USA). Cross-sectional images in a 400 x 400 \(\mu m\) area were recorded simultaneously at every mirror position of the step-scan interferometer at a spatial resolution of 6-7 \(\mu m\). Imaging spectra were recorded at 16 cm\(^{-1}\) spectral resolution, an undersampling ratio (UDR) of 4 and a mirror step rate of 1 Hz. The step distance of the interferometer at UDR 4 was 1.266 \(\mu m\). Approximately 500 interferosteps were necessary to obtain a spectral resolution of 16 cm\(^{-1}\). The low step rate (1 Hz) allows the frame grabber board in the camera to average 200 images during each step, leading to a high signal to noise ratio (S/N). A zinc selenide (ZnSe) window was used for calibration and as background spectrum. The resulting data set contained 4096 interferograms, one for every pixel in the FPA. Further data processing was conducted using Bio-Rad Win-IR Pro 2.5 software. The Kramers-Kronig transformation was applied to transform the specular reflectance spectra to absorbance-like spectra, which is easier to work with and interpret. Analytical results of the imaging FTIR system are displayed as infrared spectra and false color or gray-scale images. Every spot or pixel in the cross-section image contains an infrared spectrum. A false color or gray-scale plot shows the intensity distribution of a particular absorption band on the surface of the cross-section.

**Single-point transmission FTIR spectroscopy**

Single-point FTIR analysis was performed on the above-mentioned Bio-Rad...
Improving the surface quality of paint cross-sections for analytical imaging techniques

A spectrometer with IR microscope, and a single-point Mercury Cadmium Tellurium detector (4000-650 cm\(^{-1}\) range). The selected sample was applied onto a Graseby Specac P/N 2550 diamond cell (Graceby Specac, Orpington, Kent, UK) and analyzed in transmission mode. An empty diamond cell was used as background. All single point spectra were recorded at 4 cm\(^{-1}\) spectral resolution, an undersampling ratio (UDR) of 2 and a mirror speed of 5 kHz. A total of 100 spectra were accumulated to increase the signal to noise ratio (S/N). Data were processed using Win-IR Pro 2.5 software of Bio-Rad.

**SIMS imaging**

Secondary ion mass spectrometry (SIMS) provides detailed information on the distribution of both organic and inorganic components in a paint cross-section. The scanning of a primary ion beam over the surface of the cross-section generates secondary ions from the paint sample. A full mass spectrum is measured for every pixel (max. 1 x 1 \(\mu\)m). The static-SIMS imaging experiment was performed on a Physical Electronics (Eden Prairie, Minnesota, USA) TRIFT II time-of-flight SIMS (ToF-SIMS). The surface of the sample was scanned with a pulsed 25 keV primary ion beam from an \(^{115}\)In\(^+\) (indium) liquid metal ion gun. The pulsed beam was non-bunched with a pulse width of 1 ns. The static-SIMS imaging experiment was performed on a Physical Electronics (Eden Prairie, Minnesota, USA) TRIFT II time-of-flight SIMS (ToF-SIMS). The surface of the sample was scanned with a pulsed 25 keV primary ion beam from an \(^{115}\)In\(^+\) (indium) liquid metal ion gun. The pulsed beam was non-bunched with a pulse width of 1 ns. The static-SIMS imaging experiment was performed on a Physical Electronics (Eden Prairie, Minnesota, USA) TRIFT II time-of-flight SIMS (ToF-SIMS). The surface of the sample was scanned with a pulsed 25 keV primary ion beam from an \(^{115}\)In\(^+\) (indium) liquid metal ion gun. The pulsed beam was non-bunched with a pulse width of 1 ns. The static-SIMS imaging experiment was performed on a Physical Electronics (Eden Prairie, Minnesota, USA) TRIFT II time-of-flight SIMS (ToF-SIMS). The surface of the sample was scanned with a pulsed 25 keV primary ion beam from an \(^{115}\)In\(^+\) (indium) liquid metal ion gun. The pulsed beam was non-bunched with a pulse width of 1 ns. The static-SIMS imaging experiment was performed on a Physical Electronics (Eden Prairie, Minnesota, USA) TRIFT II time-of-flight SIMS (ToF-SIMS). The surface of the sample was scanned with a pulsed 25 keV primary ion beam from an \(^{115}\)In\(^+\) (indium) liquid metal ion gun. The pulsed beam was non-bunched with a pulse width of

![FTIR imaging data of the paint cross-section](Fig. 1.3)
20 ns, a current of 600 pA and spot size of around 120 nm. The primary ion beam was rastered over a 250 x 250 µm sample area, divided into 256 x 256 pixels. The surface of the sample was charge compensated with electrons pulsed in between the primary ion beam cycles. To prevent large variations in the extraction field over the large insulation surface area of the paint cross-section, a non-magnetic stainless steel plate with slits (1 mm) was placed on top of the sample. The cross-section was rinsed with hexane to reduce contamination of polydimethyl siloxanes. Measurements were performed in both the positive and negative modes.

**SEM-EDX**

Scanning electron microscopy studies in combination with energy dispersive X-ray analyses (SEM-EDX) were performed on a XL30 SFEG high vacuum electron microscope (FEI, Eindhoven, The Netherlands) equipped with an EDX system with spot analysis and elemental mapping facilities (EDAX, Tilburg, The Netherlands). Backscattered electron images of the cross-sections were taken at an acceleration voltage of 20 kV, at 5 mm eucentric working distance and a spotsize of 3 that corresponds to a beam diameter of 2.2 nanometer with current density of approximately 130 pA. EDX analyses were performed at a spot size setting of 4 (beam diameter 2.5 nm and current density 550 pA) to obtain a higher count rate. EDX mapping settings were 256 x 200 matrix, 512 or 1024 frames, 200µs dwell time and 17 or 35 µs amplitude time. Samples were carbon coated in a CC7650 Polaron Carbon Coater with carbon fibre (Quorum Technologies, East Sussex, UK) prior to SEM-EDX analysis to improve surface conductivity.

**DTMS**

Direct temperature resolved mass spectrometry (DTMS) is a fast fingerprinting method suitable for the characterization of classes of organic compounds particularly in tiny and complex paint samples: oils, resins, waxes, proteins, carbohydrates as well as certain pigments. The sample is heated and decomposed into characteristic molecular fragments (pyrolysis) that are measured as a function of temperature. This results in volatilization of weakly bound and low molecular weight desorbing compounds at a low temperature and subsequent pyrolysis of polymeric material at higher temperatures. DTMS analyses were performed on a JEOL SXSX102A 4-sector double-focusing mass spectrometer (JEOL-Europe, Schiphol-Rijk, The Netherlands). Samples selected with a stereo-microscope were made into a suspension in a mini-mortar using aliquots of ethanol. The suspension was transferred to the Pt/Rh filament of the insertion probe and dried in vacuum. The probe was then inserted directly into the ion source and heated. The temperature linearly increased from room temperature to approximately 800 °C in two minutes. The components released from the probe are ionized at 16eV under electron ionization (EI) conditions in an ionization chamber kept at 180 °C, and subsequently mass analyzed over the range m/z 20-1000, with a 1-s cycle time. Data were processed using a JEOL MP-7000 data system.
IMPROVEMENT OF ANALYTICAL DATA AFTER RE-POLISHING

FRANZ IGNAZ GÜNther ‘SAINT ISIDOR’ C.1765 (ABBEY CHURCH ROTT AM INN)

The paint cross-section from the flesh tone of Saint Isidor shows a thin organic intermediate layer in the paint build-up measuring 8-10 µm in thickness (Fig. 1.3b-c, layer 3). In ultra violet illumination, this layer exhibits a bluish fluorescence. Its composition and function were to be solved. Because the layer was too thin and lacked a distinctive color, we were unable to manually separate this layer from the white ground layers underneath and the pinkish paint layer on top. A first attempt to analyze the thin intermediate layer using specular reflection FTIR imaging did not provide any indication of its nature either (Figs. 1.4a-c). An area of 400 by 400 µm (= 64x64 pixels) of the cross-section surface was recorded. The processed data set contains an infrared spectrum for each pixel. Characteristic absorption bands can be selected in the spectrum and imaged as false-color plots showing their distribution in intensity in the cross-section (red = high intensity; blue = low intensity). The infrared spectrum in Fig. 1.4a represents a spot (a pixel is about 6x6 µm) in the organic intermediate layer, but the spectrum does not contain any particular absorption bands, showing merely noise and interference from the layers on top and below. Careful examination of the surface of the cross-section with the light microscope (bright field, without polarizers) revealed many deformations and scratches. It became clear that the organic layer was scoured below the surface because of its softer consistency, as compared to the adjacent pigmented layers, pointing to a wet polishing preparation. Moreover, the whole surface exhibited many non-reflecting dark spots as a result of unevenness.

After improving the surface by re-polishing, a new FTIR data file that contained relevant analytical information was recorded (Figs. 1.5a-c). Fig. 1.5a shows an infrared spectrum of the intermediate layer after re-polishing revealing characteristic proteinaceous features: a broad band assigned to N-H stretch vibration at c.3300 cm\(^{-1}\) and the combination of two strong, narrow bands at c.1643 cm\(^{-1}\) and c.1540 cm\(^{-1}\) assigned to the C=O stretch (amide I) and N-H bending (amide II) vibrations, respectively. The latter overlaps with the carboxylate peak of (converted) lead white present in the adjacent layers. The intensity of the amide I band at c.1640 cm\(^{-1}\) is plotted in the FTIR image in Fig. 1.5b: the high intensity (red stroke) represents the organic intermediate layer. Imaging the same absorption band in the data set from before re-polishing had not revealed the same concentrations in the organic layer, only noise owing to surface irregularities (Fig. 1.4b). The image of the carbonate absorption band around 1400 cm\(^{-1}\) was also significantly improved after re-polishing and displayed a more even distribution (compare Figs. 1.4c and 1.5c). When combining the FTIR results with the EDX elemental maps of lead and calcium (Figs. 1.3d-e), the presence of carbonates in layer 2 and 4 can be more precisely attributed to lead white (basic lead carbonate) and in layer 1 (ground) to chalk (calcium carbonate). This unique multi-layer structure of flesh painting is similar to other sculptures by Ignaz Günther. Indications
for the use of proteinaceous intermediate layers in the layer structure of flesh areas of polychrome sculptures are found in a Spanish treatise from the seventeenth century by Francisco Pacheco [Karbacher 2004; Richter, Schäfer and Van Loon 2006].

The presence of a proteinaceous isolation layer was confirmed by protein selective staining using Sypro® Ruby [Richter, Schäfer and Van Loon 2006; Schäfer forthcoming thesis]. These staining tests were also able to identify proteinaceous binding media in the underlying lead white (2) and chalk ground (bottom) layers (1), apart from the high concentration in the organic isolation layer. Furthermore, DTMS analysis of isolated material from the flesh layer (4) demonstrated oil components.

To date, we have only successfully identified pure protein layers in cross-sections using SR-FTIR imaging. However, we have not been able to detect protein features in pigmented protein layers containing inorganic pigments such as chalk or lead white [Van Loon and Boon 2004]. This is associated with the limitations of the specular reflection technique. The intensity of the reflected beam is related to the refractive index of the same sample as described by Fresnel’s law. Organic materials have a lower reflectance, as compared to inorganic pigments with higher refractive indices. In the common case of radiation in air striking the surface of a medium with refractive index n at normal incidence, the reflection is given by \((n-1)^2/(n+1)^2\): for an organic material with \(n=1.5\) the reflection at the surface is only 4%, while the reflection is 25% for an inorganic pigment with \(n=2\). Furthermore, a much lower content of organic material is exposed at the cross-section surface in typical ground and paint mixtures as compared to pure organic layers. For example, in a chalk/glue ground, a higher amount of chalk is present relative to animal glue (a proteinaceous material). We calculated a typical w/w chalk : glue ratio of about 20 : 1(!). Finally, the most important reason for failure may be scattering within the sample (described as sub-surface reflections), which distorts the specular reflection spectrum.
This example also demonstrates the potential of specular reflection FTIR imaging for the analysis of organic layers in paint cross-sections. We examined the thick yellowed/browned varnish in a cross-section from an orangey area in Van Gogh’s *Les Alyscamps* (Fig. 1.6). Questions about the composition of the varnish arose during cleaning tests of the painting because the varnish could not be removed with normal cleaning solvents. The cleaning was further complicated by the impasto character of the paint and the

Vincent van Gogh ‘Falling Leaves (Les Alyscamps)’ Autumn 1888 (Kröller Müller Museum inv. no. 224, F486)

Figs. 1.7 (before re-polishing) and 1.8 (after re-polishing) Light microscopic images and FTIR imaging data of the cross-section in Fig. 1.6. FTIR imaging localized the different varnish components in the cross-section.
strong sensitivity/vulnerability of the orangey yellow paint that covers large areas of the painting. Previous research demonstrated that the yellow paint is seriously affected by zinc soap aggregate formation, which has resulted in the manifestation of numerous white-translucent masses at the paint surface that have extended/protruded through the varnish in some areas [Van der Weerd et al. 2003].

Isolated samples of the varnish were analyzed using single-point transmission FTIR and DTMS. The FTIR transmission spectrum (Fig. 1.6b) reveals a mixture of natural resin (blue arrows), proteins (red arrows) and carbohydrates (green arrow). DTMS analysis under EI conditions provides evidence for the presence of mastic, a triterpenoid resin, and under CI conditions of starch, a polysaccharide. Proteins were not detected by DTMS. However, the first attempt at determining the different varnish components and their locations within the cross-section using FTIR imaging were unsuccessful, as shown in Fig. 1.7a-b. Imaging the amide I band at c.1649 cm\(^{-1}\) showed a blurred distribution of the proteinaceous material within the varnish layer.\(^5\) Examination of the cross-section surface with the light microscope (bright field, without polarizers) revealed a very roughened and uneven, low-reflecting surface.

After re-polishing the surface, we repeated FTIR imaging measurements. The new results could clearly localize the different varnish components in the cross-section and link them to observed differences in UV fluorescence within the varnish layer. Fig. 1.8d shows the infrared spectrum representing the lower parts in the varnish layer that exhibited a light-grayish fluorescence in UV. The spectrum reveals characteristic peaks of proteins, two sharp peaks at c.1649 cm\(^{-1}\) and c.1547 cm\(^{-1}\) assigned to the Amide I and II (red arrow), as well as a typical carbohydrate pattern in the 1100-1000 cm\(^{-1}\) region due to C-O stretch vibrations (green arrow) [Derrick et al. 1999]. The carbohydrate band at c.1020 cm\(^{-1}\) was difficult to image because it overlapped with strong sulfate and chromate absorption bands from the lead chromate, barium sulfate (barite) and calcium sulfate (gypsum) present in the yellow paint. Fig. 1.8f demonstrates that the highest concentrations of the 1020 cm\(^{-1}\) band occur in the underlying yellow paint layer. The FTIR image of the amide I group at c.1649 cm\(^{-1}\) (Fig. 1.8c) shows a high and uniform intensity in the lower ‘grayish’ area of the varnish. In contrast, the FTIR spectra of the upper part of the varnish, which shows a much stronger UV fluorescence, display peak characteristics of resinous material (mastic), including a strong carbonyl (C=O) stretch at c.1720 cm\(^{-1}\) and bands in the 2900 cm\(^{-1}\) region due to C-H stretch vibrations (Fig. 1.8e, blue arrows).

From the FTIR results, it is concluded that remnants of a protein and carbohydrate mixture are present on the paint surface, sitting in the interstices of the impasto paint.\(^6\) They must originate from an old restoration, probably from a facing applied to protect the paint surface during the lining process (the painting is wax-resin lined in the past). A mastic varnish was applied on top. This new information on the

---

\(^5\) The first analysis attempt was carried out by Heleen Zuurendonk (AMOLF intern 2003-04) and described in her Master thesis [Zuurendonk 2004].

\(^6\) The presence of protein confirms the conservator’s observation that the varnish is shrinking and tearing off the paint. Personal communication Luuk Struijk van der Loeff, Kröller Müller Museum Otterlo.
Improving the surface quality of paint cross-sections for analytical imaging techniques

JOHANNES VERMEER ‘DIANA AND HER COMPANIONS’ C.1655 (MAURITSHUIS INV NO 406)

In the last case study, we will discuss the SIMS experiments of a paint cross-section from Vermeer’s painting *Diana and her Companions* [Kolfin et al. 2002]. This cross-section was extensively examined in the context of research on metal soap aggregate formation [Noble et al. 2002; Weerd et al. 2002a]. It exposes the layer build-up of the foliage in the background (Fig. 1.9) showing a light ground, followed by a reddish brown underlayer, then a yellow intermediate layer with lead-tin yellow pigment that has formed metal soap inclusions, and finally a blue top layer containing smalt (blue cobalt potash glass). In SIMS experiments, a primary ion beam rasters over the surface and generates organic and inorganic secondary ions from the paint sample. Similarly, with respect to FTIR imaging, a mass spectrum is collected for each pixel (up to 1x1 µm). Hence, spatially resolved information on the elemental composition is obtained and (pseudomolecular or fragment ions of) whole molecules are detected. SIMS reveals detailed information on the composition of the metal soap inclusions situated in the yellow paint layer. These soap masses are usually too small in dimension to be isolated from the paint layer for analysis. A first attempt to analyze the composition of the layers in this cross-section gave rather poor results. We see a blurred total ion image of a selected area of the cross-section (Fig. 1.12a). Additionally, the imprint of a large scratch is visible through the smalt layer. The overall mass spectrum (Fig. 1.10) contains very noisy and broad peaks. Differences in height in the cross-section surface result in small flight time differences of the ions, resulting in peak broadening and poorly resolved mass peaks. Re-polishing the surface of the cross-section significantly improved the quality of the SIMS data. Fig. 1.13a displays the sharper total ion image acquired after re-polishing. In the same mass range, the mass resolution is improved resulting in smaller peaks (Fig. 1.11). A good example is the peak at \textit{m/z} 56. The lower mass side of this peak represents iron, which has an exact mass of 55.96; at the higher mass side, an organic fragment is detected at \textit{m/z} 56.09. In the mass spectrum obtained before re-polishing, these two peaks completely overlap and cannot be distinguished from each other (Fig. 1.10). The SIMS image of this peak visualizes some hotspots, but there is no clear relationship with the layer build-up (Fig. 1.12b). In contrast, in the mass spectrum collected after re-polishing (Fig. 1.11), the two bands are well-resolved. The iron and organic fragment ions are plotted as separate layers (Figs. 1.13b-c): the highest concentration of iron occurs in the reddish brown underlayer, which supports the presence of red ochre in this layer, while the organic fragment is more abundant in the yellow layer, which is richer in oil paint medium. The detection of lead palmitate (\textit{m/z} 461-63) and lead stearate (\textit{m/z} 489-91) in the yellow layer (Fig. 1.13d) confirms the formation of lead soap aggregates, and complements the earlier FTIR and SEM-EDX analyses [Noble et al. 2002; Weerd et al. 2002a]. The deposition of discrete tin particles outside the soap masses (Fig. 1.13e) corresponds to observations reported on other
Chapter 1

examples of saponified lead tin yellow paints [Boon et al. 2004]. The map of cobalt \((m/z 59)\) was also greatly improved after re-polishing the surface and now overlaps better with the distribution of smalt particles in the top layer (compare Figs. 1.12c and 1.13f).

Figs. 1.10 (before re-polishing) and 1.11 (after re-polishing) Selected areas of the overall SIMS mass spectra of the paint cross-section from Fig. 1.9.

**DISCUSSION AND CONCLUSIONS**

The three case studies discussed in this paper illustrate the importance of surface preparation of paint cross-sections for successful application of analytical imaging techniques. For specular reflection FTIR imaging, the reflecting surface must appear bright, or mirror like, when viewed with the microscope in incident light (unpolarized). Dark lines and spots are indicative of surface irregularities. SIMS is also a surface sensitive technique: secondary ions are generated from the upper atomic layers of the cross-section. Hence, it is to be expected that even very small height differences in the surface and other irregularities in the surface negatively influence the analytical results.
Figs. 1.12 (before re-polishing) and 1.13 (after re-polishing) SIMS images of the paint cross-section in Fig. 1.9.
Chapter 1

We suggest a careful estimation of the surface beforehand to evaluate data reliability and help with data interpretation. A good method of evaluating surface quality and observing surface irregularities was to examine the specimen surface with the light microscope in bright field without polarizers (Fig. 1.14). In this manner, specular reflection of the sample is observed.

We also noticed that normal light microscopy and SEM-EDX benefit from surface improvement. In normal light microscopy, a poor surface is partly compensated by saturating the surface with mineral spirits or by using polarizing filters that reduce light scattering and promote image optimization. An absolute plane surface, however, helps with layer interpretation and provides sharper images. The same applies to SEM-EDX analysis. We noted that a higher surface quality enables higher magnification and leads to sharper BSE images and higher spatially resolved elemental mappings.

In our experience, dry polishing the sample as well as the use of a polishing holder to provide even pressure on the sample during polishing are very essential factors to achieving truly plane surfaces. The other factors considered in the paper such as making short straight movements and the use of clean sheets help to further minimize surface artifacts and chemical modifications of the specimen surface. The dry polishing method can be used to prepare new samples, but the three case studies presented in this paper have shown that it can also be applied to improve the surfaces of existing cross-sections and obtain relevant analytical information.

Acknowledgements

We would like to thank René Koper, Surface Preparation Laboratory, Zaandam, for his useful tips and discussions on surface preparation. Glen van Vugt, Struers GmbH Nederland, Maassluis, and Jan Blonk, 3M Nederland BV, Zoeterwoude, have been very helpful with demonstrating and supplying polishing test sheets. We would also like to thank Mark Richter, Technische Universität München, as well as Luuk Struijk van der Loeff, Kröller Müller Museum, Otterlo, and Carol Pottasch, Royal Picture Gallery.

Fig. 1.14 Light microscopic images of a cross-section from a ceiling of the Johan de Witt House (see Chapter 4). Normal light (left). The same cross-section viewed in Bright Field without polarizers showing the irregularities in the surface: dark lines and spots (right).
Mauritshuis, The Hague for providing the paint cross-sections. SIMS measurements were performed by Katrien Keune, FOM Institute AMOLF.

REFERENCES


The Relationship between Preservation and Technique in the Paintings of the Oranjezaal

ABSTRACT – This chapter describes natural ageing processes in the seventeenth-century oil paintings of the Oranjezaal ensemble in the Royal Palace of Huis ten Bosch (The Hague). Degradation of a wide range of pigments – lead white, lead-tin yellow, red lead, smalt, azurite, blue verditer, verdigris, ultramarine, vivianite, orpiment, vermilion, bone black, schiet-yellow, red lake, indigo and Kassel earth – in oil paints is discussed. In this unique case of an ensemble of paintings kept under known conditions and with similar restoration histories, it was possible to relate the degree of ageing to differences in quality of pigment and binding medium and the ways in which the artists applied their materials.

INTRODUCTION

The Oranjezaal is the central hall of the seventeenth-century Royal Palace of Huis ten Bosch in The Hague, Netherlands [Loonstra 1985]. It houses a unique Baroque ensemble consisting of 30 large-scale canvas paintings on two levels integrated into the painted architecture and a further nine painted directly on the wooden vaults and doors, glorifying the life of stadholder Frederik Hendrik (Fig. 2.1). The paintings were made between 1648 and 1652 by 12 prominent artists from the northern and southern Netherlands for Amalia van Solms, who had decided to dedicate the Oranjezaal to the memory of her suddenly deceased husband (Table 2.1). She, together with Constantijn Huygens and Jacob van Campen, conceived the decorative scheme. To establish the unity, each artist was instructed about composition and was given primed canvases. The paintings have hung together in the room ever since1 and have a similar, known restoration history that comprises very few interventions.2 This uniformity means that the only variables are style, painting technique and choice of materials by the artists themselves.

The recent restoration of the Oranjezaal ensemble offered a unique opportunity to study different material and ageing properties of the paints. Nearly all pigments in oil paint show some degree of deterioration as a result of pigment-medium interactions, migration/diffusion of mobile components, oxidation reactions, drying and rheology problems, and/or photochemical reactions. Although many factors may influence the

1 Except during World War II, when all paintings were moved to a bunker in Paaslo for safety [Van der Heiden 1997]. Apart from these five years, they have remained in situ, although some have changed from position in the room.
2 In this unique situation, much archival information on earlier treatments was found that could be related to still visible traces of intervention on the paintings, specifically traces of old varnish that were found behind the frames. They could be identified and linked to the previous treatments. The varnish has been removed only three times, which is far less than what is common for seventeenth-century paintings. The first varnish removals date from 1767 (by Jan van Dijk) and 1806 (by Huijbrechts). After that date, the restorations were restricted to surface cleaning and (local) re-varnishing [Te Marvelde 2005]. The last removal was during its recent restoration (1998-2001).
ageing processes in the paint, namely the materials, the artist's working methods, as well as age, the environment (humidity, temperature, light and pollutants) and conservation history, it was essentially the initial choices of materials and how they were applied that accounted for the observed differences in degradation, since the oil paintings were kept under comparable, known, conditions and have a similar history. This made it possible to deduce whether a process was due to the inappropriate use of material by one painter, was inherent to the material and therefore present in all the paintings, or was dependent on the quality of the pigment and medium chosen. Valuable insight was obtained into natural ageing processes, materials and seventeenth-century Netherlandish painting practice.

**Analytical Methods**

The degree of preservation of the paintings was evaluated by combining examination of the painting surfaces and studies of paint cross-sections with chemical analysis of paint samples. Nearly 500 paint cross-sections were taken to study the painting technique and degradation effects, of which about 200 were further examined using scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX), specular reflection Fourier transform infrared (FTIR) imaging, secondary ion mass spectrometry (SIMS) and/or Raman microscopy. Furthermore, samples of the grounds of all 30 canvases were analyzed using direct temperature resolved mass spectrometry (DTMS). The binding medium of a selection of samples of white and dark areas was determined by online trans-methylation pyrolysis gas chromatography / mass spectrometry (Py-TMAH-
High performance liquid chromatography (HPLC) was carried out to identify the dye components of the organic lake pigments. Binding medium analyses using mass spectrometric techniques, DTMS and GC/MS, were performed at the FOM Institute AMOLF by Ester Ferreira and Jerre van der Horst. All red lakes were analyzed at KIK-IRPA (Royal Institute for Cultural Heritage) in Brussels by Jan Wouters. Some of the yellow lake pigments were measured at ICN (Netherlands Institute for Cultural Heritage) in Amsterdam by Maarten van Bommel.
Fig. 2.2 Jacob Jordaens, *Frederik Hendrik in Triumph*, 1652, Oranjezaal No. 32. Overall, and detail of the now dull-gray saddle-cloth of Willem II (lower right) as a result of smalt degradation. Photo (painting): Royal Collections. Photo (detail): SRAL.

Fig. 2.3 Pieter de Grebber, *Part of the Triumphal Procession with Spoils of War*, 1648, Oranjezaal No. 24. Overall, and detail showing the whitened dark brown boots of the boy at right. Photo (painting): Royal Collections.
Chapter 2

Effect of ageing on the overall appearance

Due to natural ageing, all pictures have changed in appearance, some more obviously than others. For the viewer, the most disturbing color changes include the blackening of red vermilion, the whitening of dark areas containing bone black, and the alteration of the blue color in smalt-containing areas to give a brown, gray transparent, and/or cracked surface appearance. These changes not only disturb the modeling locally,

Table 2.1 List of paintings from the Oranjezaal ensemble

<table>
<thead>
<tr>
<th>nr</th>
<th>artist</th>
<th>title</th>
<th>support</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Caesar van Everdingen</td>
<td>Allegory on the birth of Frederik Hendrik</td>
<td>canvas</td>
</tr>
<tr>
<td>2, 37</td>
<td>Jacob van Campen</td>
<td>Apollo in the sun-chariot preceded by the rosy-fingered dawn</td>
<td>wood (vault)</td>
</tr>
<tr>
<td>3</td>
<td>Jan Lievens</td>
<td>Five muses</td>
<td>canvas</td>
</tr>
<tr>
<td>4</td>
<td>Caesar van Everdingen</td>
<td>Four muses</td>
<td>canvas</td>
</tr>
<tr>
<td>5</td>
<td>Theodoor van Thulden</td>
<td>The smithy of Vulcan</td>
<td>canvas</td>
</tr>
<tr>
<td>6</td>
<td>Theodoor van Thulden</td>
<td>Venus in the smithy of Vulcan</td>
<td>canvas</td>
</tr>
<tr>
<td>7</td>
<td>Christiaan van Couwenbergh</td>
<td>The young Hercules strangling two snakes in his crib</td>
<td>canvas</td>
</tr>
<tr>
<td>8</td>
<td>Christiaan van Couwenbergh</td>
<td>The young Hyro being fed by bees</td>
<td>wood (chimney)</td>
</tr>
<tr>
<td>9</td>
<td>C. S. Cuylenborg</td>
<td>War trophies (addition of 1806)</td>
<td>wood (chimney)</td>
</tr>
<tr>
<td>10</td>
<td>Theodoor van Thulden</td>
<td>The education of Frederik Hendrik</td>
<td>canvas</td>
</tr>
<tr>
<td>11</td>
<td>Thomas Willeboirts Boschaert</td>
<td>Frederik Hendrik and Maurits in the field</td>
<td>canvas</td>
</tr>
<tr>
<td>12</td>
<td>Gerard van Honthorst</td>
<td>Allegory on the marriage of Frederik Hendrik and Amalia van</td>
<td>canvas</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solms</td>
<td></td>
</tr>
<tr>
<td>13, 38</td>
<td>Caesar van Everdingen</td>
<td>Allegory on heavenly and earthly love</td>
<td>wood (vault)</td>
</tr>
<tr>
<td>14</td>
<td>Theodoor van Thulden</td>
<td>Dutch maiden offering Frederik Hendrik the supreme command</td>
<td>canvas</td>
</tr>
<tr>
<td>15, 35</td>
<td>Pieter Soutman</td>
<td>Allegory on the excellent rule of Frederik Hendrik</td>
<td>wood (vault)</td>
</tr>
<tr>
<td>16</td>
<td>Thomas Willeboirts Boschaert</td>
<td>Frederik Hendrik as lord of the seas</td>
<td>canvas</td>
</tr>
<tr>
<td>17</td>
<td>Gerard van Honthorst</td>
<td>Frederik Hendrik's steadfastness</td>
<td>canvas</td>
</tr>
<tr>
<td>18</td>
<td>Jacob van Campen</td>
<td>Frederik Hendrik in battle commanding the waters</td>
<td>canvas</td>
</tr>
<tr>
<td>19</td>
<td>Gonzales Coques</td>
<td>Frederik Hendrik receiving survivance for Willem II</td>
<td>canvas</td>
</tr>
<tr>
<td>20</td>
<td>Gerard van Honthorst</td>
<td>The arrival of Mary greeted by Willem II</td>
<td>canvas</td>
</tr>
<tr>
<td>21</td>
<td>Gerard van Honthorst</td>
<td>Allegory on the marriage of Louise Henriette and the Grand</td>
<td>canvas</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Monarch of Brandenburg</td>
<td></td>
</tr>
<tr>
<td>22, 36</td>
<td>Pieter de Grebber</td>
<td>The ascension of Frederik Hendrik into heaven</td>
<td>wood (vault)</td>
</tr>
<tr>
<td>23</td>
<td>Theodoor van Thulden</td>
<td>Part of the triumphal procession with prisoners</td>
<td>canvas</td>
</tr>
<tr>
<td>24</td>
<td>Pieter de Grebber</td>
<td>Part of the triumphal procession with spoils of war</td>
<td>canvas</td>
</tr>
<tr>
<td>25</td>
<td>Salomon de Bray</td>
<td>Part of the triumphal procession with captured weapons</td>
<td>canvas</td>
</tr>
<tr>
<td>26</td>
<td>Salomon de Bray</td>
<td>Part of the triumphal procession with musicians</td>
<td>canvas</td>
</tr>
<tr>
<td>27</td>
<td>Pieter Soutman</td>
<td>Part of the triumphal procession with prize gold and silver</td>
<td>canvas</td>
</tr>
<tr>
<td>28</td>
<td>Pieter de Grebber</td>
<td>Part of the triumphal procession with sacrificial bull</td>
<td>canvas</td>
</tr>
<tr>
<td>29</td>
<td>Theodoor van Thulden</td>
<td>Part of the triumphal procession with elephant and paintings</td>
<td>canvas</td>
</tr>
<tr>
<td>30</td>
<td>Jacob van Campen</td>
<td>Part of the triumphal procession with gifts from East and West</td>
<td>canvas</td>
</tr>
<tr>
<td>31</td>
<td>Gerard van Honthorst</td>
<td>Part of the triumphal procession, Amalia with her daughters</td>
<td>canvas</td>
</tr>
<tr>
<td></td>
<td></td>
<td>observing the victory</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>Jacob Jordaens</td>
<td>Frederik Hendrik in triumph</td>
<td>canvas</td>
</tr>
<tr>
<td>33</td>
<td>Jacob Jordaens</td>
<td>Allegory on time</td>
<td>canvas</td>
</tr>
<tr>
<td>34</td>
<td>Christiaan van Couwenbergh</td>
<td>Minerva and Hercules opening the doors for victory</td>
<td>wood (door)</td>
</tr>
<tr>
<td>39</td>
<td>Jacob van Campen, Pieter</td>
<td>Sky with cherubs on the wing, holding the portrait of Amalia van</td>
<td>wood (cupola)</td>
</tr>
<tr>
<td>Soutman, Pieter de Grebber,</td>
<td></td>
<td>Solms</td>
<td></td>
</tr>
<tr>
<td>Cesar van Everdingen</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>Gerard van Honthorst</td>
<td>Amalia van Solms as a widow</td>
<td>wood (cupola)</td>
</tr>
<tr>
<td>43</td>
<td>Christiaan van Couwenbergh</td>
<td>Herald (southwest)</td>
<td>canvas</td>
</tr>
<tr>
<td>44</td>
<td>Christiaan van Couwenbergh</td>
<td>Herald (southeast)</td>
<td>canvas</td>
</tr>
<tr>
<td>45</td>
<td>Christiaan van Couwenbergh</td>
<td>Herald (northeast)</td>
<td>canvas</td>
</tr>
<tr>
<td>46</td>
<td>Christiaan van Couwenbergh</td>
<td>Herald (northwest)</td>
<td>canvas</td>
</tr>
<tr>
<td>47-50</td>
<td>Christiaan van Couwenbergh</td>
<td>Paneling with weaponry</td>
<td>wood (windows)</td>
</tr>
</tbody>
</table>
but sometimes also affect the color harmony in the whole composition. For example, the dull gray saddle-cloth on the horse of Willem II in *Frederik Hendrik in Triumph* by Jordaens (No. 32) contains smalt and must have been originally bright blue; thus, instead of accentuating the importance of this figure in the painting, the grayed saddle-cloth now makes him recede into the background (Fig. 2.2). On the contrary, a pair of dark-brown leather boots in a shadow area of one of the *Triumphal Processions* by De Grebber (No. 24) is affected by whitening; therefore this rather unimportant detail is optically brought forward/to the fore in the composition (Fig. 2.3). In the other *Triumphal Procession* by De Grebber (No. 28), the rather monotone upper right half, showing a flag painted with the blue earth pigment vivianite, which has turned gray, now strongly contrasts with the bright blue-, yellow- and red-colored areas in the rest of the painting (Fig. 2.8). Less obvious, but very disrupting for the modeling, is the fading of red lake pigments in draperies, since the lake will retain its color in the thickly painted shadows, but loses it in the mid-tones, resulting in more abrupt light-dark contrasts than originally intended. Occasionally, the original color is preserved behind the frame, as is the case with the face of a girl in Van Thulden’s *Triumphal Procession with Elephant and Paintings* (No. 29). Where the paint with lead white and a light-sensitive red lake is exposed, the face looks rather pale, but behind the frame the original bright pink paint is retained (Fig. 2.4). Lead-containing pigments are known to interact with the oil medium, which leads to the formation of lead carboxylates/soaps. Several degradative phenomena that affect the appearance of the paint surface are associated with lead soap formation: aggregates, efflorescence and increased transparency [Noble, Van Loon, Boon 2005]. Increased transparency of paints containing lead white is mainly noticed in the case of compositional changes. Also, in some paintings, the background seems somewhat darkened, making certain elements difficult to discern; this might also be an effect of increased transparency. In red and yellow lead-containing paints, rather the surface texture has changed as a result of the formation of lead soap aggregates.

Although these chemical changes occur in all paintings, many have hardly suffered from physical changes owing to the high-quality preparation of the canvases and to minimal interventions. This will be described in more detail in the next section.

SUPPORTS AND PREPARATION LAYERS

The majority of the paintings are still fixed with strings to their original strainer. The canvas supports are of high quality and are in good condition and the seams can hardly be seen from the front, partly owing to an extra ground layer. As few as four paintings are wax-resin lined (Nos. 10, 12, 19 and 20), which is exceptionally low compared to other collections. Only on a few canvases can traces of water damage and/or repair

---

8 Although not examined here in great detail, these brown and gray mid-tones are usually mixtures of lead white and pigments that absorb a large portion of oil, such as black pigments, earth pigments and red lakes. The dissolution of lead white, which readily reacts with an excess of fatty acids forming lead carboxylates, results in a darker appearance of the paint. This phenomenon is described in Chapter 5.
Fig. 2.5 Beige-colored ground seen from the side of the canvas (upper left). Light microscopic (upper right) and SEM backscatter images (lower left and right) of an ion-milled cross-section from the ground showing the high packing density of the lead white in the ground.

Fig. 2.4 Detail of Theodoor van Thulden, *Part of the Triumphal Procession with Elephant and Paintings*, 1651, Oranjezaal No. 29. The pinkish color of the flesh containing light-sensitive red lake mixed with lead white has been preserved in the part covered by the frame. Photo: SRAL.
patches be seen on the back. In contrast, the wooden supports have suffered more significant damage over the course of time: the individual planks have shrunk causing narrow openings, which disturb the pictorial illusion.

According to a contract that has survived, the canvas supports were prepared with a uniform, light beige-colored ground by the primer François Oliviers. The wooden elements in the room were given a chalk-glue preparation followed by a light-gray ground. The composition of the priming layers of the 30 canvases was studied thoroughly. The sizing layer on the canvas consists of pure animal glue. The grounds,

---

9 The Royal Archives, The Hague, keeps the contract from 1647 that was made with the primer François Oliviers [Van Gelder 1948-49].

10 During the preliminary research, the mineral composition of the ground layers was studied by Karin Groen and Annelies van Loon; light microscopic and SEM images of the ground layers were visually compared [Groen and Van Loon 1999]. Binding medium analysis of the ground layers was started by Gisela van der Doelen and completed by Ester Ferreira [Ferreira 2004].

11 DTMS analysis of the sizing layer (sample HTBS 17A5) shows mass peaks at m/z 70, 154, characteristic of animal glue (collagen). A small piece was also selected for FTIR transmission in the diamond cell. The FTIR spectrum reveals absorption bands characteristic of proteins: a broad N-H stretch band at 3300 cm⁻¹ and the combination of two strong, narrow bands at around 1650 cm⁻¹ and 1550 cm⁻¹ corresponding to the C=O stretch (amide I) and N-H bending (amide II) vibrations, respectively. No indication for admixture of starch was found in the DTMS or in the FTIR spectra.
applied in one or two sublayers, are composed of lead white in linseed oil\textsuperscript{12} with small additions of brown umber.\textsuperscript{13} In a few random cases, the lead white is mixed with chalk (Nos. 1, 25, 29 and 30), which may point to the use of the cheaper variety \textit{lootwit} rather than \textit{schulpwit} \cite{Van de Graaf 1958: 34-35}. Backscattered electron images from the SEM reveal a wide distribution of the lead white particle sizes (coarse and fine particles) and a high packing density, characteristic of seventeenth-century Dutch stack processed lead white and comparable to the lead white in the surface paint and impasto \cite{Groen 1997; Ferreira et al. 2005} (Fig. 2.5). The grounds are in good condition showing no signs of significant dissolution of the lead white or aggregate formation, features that could have caused an overall darkening of the paintings or ‘gritty’ surfaces. DTMS analysis shows that the binding medium content of the ground samples is very low compared to the pigment content.\textsuperscript{14} This relatively low organic content may explain the good condition of these grounds, because lead white readily reacts with an excess of fatty acids to form lead carboxylates \cite{Keune 2005}.

The canvas and preparation of one painting differs from the others. From historical documents, it is known that the commission for \textit{Frederik Hendrik and Maurits in the Field} (No. 11) went first to Caspar de Crayer \cite{Slothouwer 1945}. When he later refused to produce the painting, the commission was given to Thomas Willeboirts Boschaert, who was also asked to paint \textit{Frederik Hendrik as Lord of the Seas} (No. 16); however, it seems that he received only one canvas from Oliviers. Instead of a single beige-colored ground, the latter painting has a double ground consisting of a chalk-based ground\textsuperscript{15} with a light-brown oil layer on top (Fig. 2.6). The light microscopic and SEM backscatter images reveal small protrusions around red lead particles at the interface of the two ground layers. This painting shows severe deformations in the canvas and adhesion problems of the paint (Fig. 2.6). As the other canvases in the room do not show similar problems, it was concluded that these are related to this problematic support, probably mainly due to the (hydrophilic) chalk ground. The effect of the increased transparency of the upper layers is also most obvious in this painting since,

\textsuperscript{12} Py-TMAH-GCMS of the ground samples clearly identifies the binding medium as a drying oil (A:S ratio > 1). The ratios of the peak areas of the palmitic and stearic acids (P:S ratio) is typically between 1.1 and 1.2, characteristic of linseed oil. Beeswax was also detected but it is not believed to be a constituent of the binding medium as it was also detected in extracts from a sample of a wooden frame and all ground samples were collected from the side of the canvas. DTMS analysis reveals the presence of fatty acids in free, acylglyceride and lead carboxylate forms. In combination with PCA (principle component analysis), DTMS confirmed the overall resemblance in organic composition of the ground samples.

\textsuperscript{13} According to Van de Graaf, this is a common priming technique in the seventeenth century, and gives a well-dried layer, since both lead white and umber accelerate the drying process of the oil. \cite{Van de Graaf 1958: 26}.

\textsuperscript{14} This was deduced from the TIC (total ion current) chromatograms. The lead white and chalk events are significantly higher than those of the oil medium.

\textsuperscript{15} DTMS analysis of this ground (sample 16GR1) identifies the binding medium as linseed oil (Gisela van der Doelen, August 2000). In the desorption part of the total mass spectrum, which is the low-temperature region, mass peaks were observed at \textit{m/z} 256 and 284, which are characteristic of palmitic acid (C16FA) and stearic acid (C18FA), respectively. In the pyrolysis part of the total mass spectrum, which is the higher temperature region, the typical pattern of the pyrolysis products of the oil paint network were present with mainly aromatic compounds (e.g. \textit{m/z} 91, 105).
compared to the light-beige preparations, its relatively dark ground has a stronger visual impact when it becomes partly visible through the overlying paint.

**Influence of Quality of Pigment on Preservation**

Like the preparation of panels and canvases, the production of pigments and other painting materials was the work of specialists in the seventeenth century. The artists bought their materials at an apothecary’s shop or at a grocer or colorman [Levy-Halm 1998; Kirby 1999]. The pigments commonly available in the seventeenth century included the naturally occurring mineral pigments, such as the blue pigments ultramarine, azurite and vivianite, and the earths, including the yellow and red ochres and siennas, umber and Kassel earth. They still needed some preparation or refinement before use. The manufactured pigments were vermilion, lead white, lead-tin yellow, red lead, smalt, verdigris and blue verditer. There were the red and yellow lakes, complexed dyestuffs of plant or insect origin; the blue plant dyestuff indigo; and, finally, the various carbon-based blacks. There was a lively trade in painting materials in and outside the Netherlands. The Dutch were famous for their production of high-quality lead white, vermilion and smalt. Some pigments were by-products of other industries, such as lead-tin yellow, which was used in the ceramics/pottery industry. Likewise, the organic colorants were employed in the dying of textiles.

So, the supply of painting materials was very diverse and the artists could be selective in their choice of materials [Levy-Halm 1998]. When studying the different paint degradation phenomena in the Oranjezaal paintings, it appears that in many cases, there is a clear relationship between the degree of deterioration and the quality of the materials used. Most materials are not homogeneous and there are differences in quality depending on the source and manufacture, which may affect the stability. In this section, the influence of the particle size (smalt, vivianite), the production process (bone black, lead-tin yellow, red and yellow lakes) and adulterations (vermilion/red lead) will be discussed. In some cases, it also appears that artists started to replace vulnerable materials for more stable ones in their search for permanence (verdigris/blue verditer).

**Smalt**

Smalt is a blue, cobalt-containing potash glass. The pigment was available in different grades from pale gray to deep blue, with the color being dependent on the cobalt content and particle size [Muhlethaler and Thissen 1993]. Like in most seventeenth-century paintings, it was extensively used in the Oranjezaal paintings, in the skies, textiles and in the greenery. However, smalt is not a very stable pigment in oil paint, and nearly all the smalt paints in the Oranjezaal have discolored. In particular, smalt with high potassium/low lime glass composition is considered unstable, as used in the Oranjezaal paintings, and the degraded paints look gray, brownish and/or transparent now (Fig. 2.2). Discoloration is the result of potassium leaching from the potash glass by interaction with the oil medium, which lowers the basicity of the glass to such a level that the coloring component, cobalt, loses its blue color. The cobalt (II) ions
change from a tetrahedral coordination (which is blue) to an octahedral coordination state (which is light pinkish) [Boon et al. 2001]. Potassium soaps are also detected in deteriorated smalt paint films; they migrate towards the surface and add to the gray-brown appearance that is so typical of degraded smalt [Spring et al. 2005]. Although contemporary sources demonstrate that artists knew that smalt oil paints would turn brownish over time, this was generally ascribed to discoloration of the binding medium. It seems that they were not aware at the time of discoloration of the smalt pigment itself.

The different smalt compositions were analyzed using SEM-EDX. The smalt was composed mainly of silica, along with variable amounts of potassium and cobalt. Small percentages of iron, arsenic, nickel and bismuth associated with the type of cobalt ore used during this period [Muhlethaler and Thissen 1993], as well as traces of aluminum and calcium depending on the glass composition or manufacturing process, were also detected. Degradation of the smalt particles was deduced from its color loss and from the low levels of potassium in the particles measured using semi-quantitative EDX analysis, which was less than 1 wt% in the discolored particles as opposed to 10-15 wt% in intact smalt. Not much variation in the smalt elemental compositions was encountered, but rather, a variation in particle size was observed. In general, it is noted that the particle size influences the rate of discoloration: the larger particles had remained blue whereas the smaller particles in the same cross-section had already lost their color because of their stronger interaction with the oil matrix. Interestingly, the only well-preserved pure smalt paint, in the medallion in Van Honthorst’s Frederik Hendrik’s Steadfastness (No. 17), contains relatively large particles (up to 50 µm across) (Fig. 2.7). Here, the amount of potassium inside the particles is lower but is (still) above

---

16 Smalt oil paint is difficult to handle and easily forms an oilskin. According to the treatises, painters tried to absorb the surplus oil in an effective manner, either by covering the wet paint with blotting paper, or treating the ground with pinpricks to create an absorbing ground. They were also advised to leave a painting with wet smalt paint to dry horizontally or face down. [Van Eikema Hommes 2004: 26-27].
Fig. 2.8 Pieter de Grebber, *Part of the Triumphal Procession with Sacrificial Bull*, 1650, Oranjezaal No. 28. Vivianite was identified in the now gray upper layer of the right flag (left). The SEM backscatter image of the paint cross-section shows the fine particle distribution of the vivianite layer (lower right). Photo (painting): Royal Collections.

Fig. 2.9 Blue pulverant vivianite on clay substrate, from a bog in Samerberg (Bavaria), Germany. Photo: M. Richter, Technical University Munich.

Fig. 2.10 EDX spectrum of the vivianite paint in Fig. 2.8 showing the elements phosphorus (P) and iron (Fe).
the critical concentration for color loss.\textsuperscript{17} Though coarse smalt is more durable, it is more difficult to paint with compared to finely ground smalt. This is probably why it is confined to a very small area: the medallion covers no more than 10 cm\textsuperscript{2}. Apart from the quality of smalt, we have also seen that the paint matrix surrounding the smalt particles influences the degree of the deterioration observed in the smalt paints, but this will be discussed later/further in a sub-section under painting technique (see the admixture of lead white).

**VIVIANITE**

De Grebber, De Bray, Van Campen and Van Thulden used the blue earth pigment vivianite, a hydrated iron phosphate mineral, in some of the blue areas as well as in the mixed greens (Fig. 2.8).\textsuperscript{18} Interestingly, vivianite was also used in the undermodeling layer of the blue skirt (with ultramarine on top) in Van Campen’s *Triumphal Procession with Gifts from East and West* (No. 30) (Fig. 2.30). In all cases, the paints look degraded and now have a grayish/yellowish/brownish appearance instead of the original blue or green color. The effect is worst in the foliage of the paintings by De Grebber and Van Thulden, where vivianite is mixed with a yellow lake, which also has the tendency to turn gray. In Van Thulden’s *Triumphal Procession with Elephant and Paintings* (No. 29), the yellow lake was identified as weld by M. van Bommel (Fig. 2.25).\textsuperscript{19}

Although its occurrence in seventeenth-century Dutch oil paintings has only been recently noticed\textsuperscript{20}, the use of vivianite is certainly not surprising. It could be found in organic, phosphate rich environments such as peat bog iron ores and sedimentary deposits in the Netherlands, Germany and Flanders (Fig. 2.9) [Richter 2007].\textsuperscript{21} Its blue

\textsuperscript{17} Generally, well-preserved smalt contains 10-15 wt% KO\textsubscript{2}. In completely discolored smalt, KO\textsubscript{2} is below 1 wt%. Semi-quantitative EDX analysis measured percentages of potassium in the blue, coarse smalt particles of the medallion in the order of 5-8 wt%. Cobalt is detected at 3-3.5 wt%. Also traces of arsenic, iron, nickel and bismuth were detected in the smalt which are typical of the cobalt ore used in that period [Muhlethaler and Thissen, 1993].

\textsuperscript{18} De Grebber used vivianite in the green leaves (Nos. 24 and 28), and unmixed in the gray-blue flag (No 28). In De Bray’s *Triumphal Procession with Musicians* (No. 26), pure vivianite was found in the jacket of the drummer and mixed with azurite in the bluish jacket of the violin player, but not in the leaves. Van Campen’s *Triumphal Procession* (No. 30) revealed vivianite in the undermodeling layer of the blue skirt. Van Thulden used vivianite in the foliage (Nos. 6, 10 (mixed with azurite) and 25) and in the green skirt of Minerva (No. 10).

\textsuperscript{19} An area of a green-yellow leaf near the border of the painting that was covered by the frame and was relatively well preserved was sampled for analysis. The HPLC-PDA chromatogram identifies luteolin and apigenin, which are characteristic components of weld, *Reseda luteola* L, a natural flavonoid yellow dye. SEM-EDX of a cross-section of the same area detected primarily calcium in the yellow particles, and only minor traces of aluminum, suggesting that the dyestuff was mainly precipitated on a chalk substrate. See also the sub-section on red and yellow lakes.

\textsuperscript{20} The use of vivianite in Dutch seventeenth-century paintings was first reported by M. Spring in blue and mixed green areas of eight landscape paintings by Aelbert Cuyp. Recently, other examples have emerged indicating that vivianite was more commonly used in Dutch seventeenth century than had previously been thought. In Rembrandt’s *Susanna*, 1636, vivianite was identified in the foliage areas [Noble and Van Loon 2005]. Spring has also identified vivianite in two paintings by Carel Fabritius in the National Gallery London, *A View of Delft with a Musical Instrument Sellers Stall*, 1652, and *Self Portrait*, 1654 [Duparc 2004]. Furthermore, vivianite was found in Johannes Vermeer’s *The Procuress*, 1656, from Dresden, Gemäldegallerie Alte Meister [Stege et al. 2004] and more recently in works by Gerard Dou, *The Praying Anchorite*, 1646, and Cornelisz van Poelenburgh, *Adoration of the Shepherds*, around 1650, from the Alte Pinakothek Munich [Personal communication Heike Stege, Doerner Institute Munich, 2006]. The vivianite in all examples mentioned above looks degraded and shows similar particle morphology.

\textsuperscript{21} There was an active peat industry in the Netherlands [Spring 2001, note 47].
color results from an iron(II) / iron(III) interaction (intervalence charge transfer) under the absorption of light. The color varied according to the deposit itself, how it occurred, as well as how it was prepared and how long it was ground. The blue pulvérant has to be washed to remove the clay and organic residues. Subsequent grinding of the pigment (in oil or in water) introduces heat and increases the exposure to oxygen, which may further intensify the color.22 The blue color deepens with increased exposure to air, then becomes gray and is brown/yellow/orange in its fully oxidized state [Nassau 1983]. The color loss of vivianite presumably arises from a shift in the balance from iron(II) (ferrous) to iron(III) (ferric) as a result of oxidation. As reported in the literature, it may convert to the mineral metastavivanite23, which has an intermediate composition, or alternatively to santabarbaraite24, an X-ray amorphous yellow-brown product that results from complete oxidation, but this still needs to be confirmed in paintings.

In the cross-sections examined, the very small grayish particles of vivianite were hardly discernable (Fig. 2.8). This explains why the presence of vivianite may often have been overlooked in Dutch pictures. Some of the vivianite layers in fact exhibited a yellowish hue that may have become even more yellowed over time due to exposure to air (since it is very reactive to oxygen) [compare Hanzel et al. 1990]. The presence of vivianite only became apparent after SEM-EDX analysis demonstrated the exclusive presence of the elements iron (Fe) and phosphorus (P) (Fig. 2.10). The alteration of vivianite to a yellow color was also observed in cross-sections of a medieval wall painting in England [Howard 1995]. It is notable that the vivianite used in the Oranjezaal paintings and in other seventeenth-century Dutch oil paintings has a particularly fine particle distribution (particle size is about 1 µm) unlike the examples found in German polychrome sculpture, which have preserved their blue color and demonstrate a larger particle size.25 Hence, the quality and particle size of the pigment seems to relate to the available local sources where it was mined. It is also possible that vivianite in an oil medium is more prone to oxidation compared to other binding media (we don’t know the binding media of the German works). Certainly, the fine particle size increases the rate of oxidation, due to the larger surface area for oxidation to take place. Documentary sources mention various synonyms that might have been used for vivianite, of which the names ‘terra de Harlem’ or ‘Harlems Oltramarin’ point directly to the presence of a local

---

22 Two oxidation processes can take place: oxidation by oxygen diffusing into the vivianite from outside and auto-oxidation by decomposition of bound water [Hanzel et al. 1990]. The last reaction will occur at higher temperatures (between 65-315 °C), but the first one at room temperature when the mineral is exposed to air, with the iron oxidizing from the Fe(II) to the Fe(III) oxidation state: \(4\text{Fe}^{2+}\cdot(\text{PO}_4)_2\cdot8\text{H}_2\text{O} + 3\text{O}_2 \rightarrow 4\text{Fe}^{3+}\cdot(\text{PO}_4)_2(\text{OH})_3 + 26\text{H}_2\text{O}\).

23 Metastavivanite is a triclinic hydrated iron(II)-iron(III) hydroxy phosphate whose formula may be given as \(\text{Fe}^{3+}_x(\text{PO}_4)_2(\text{OH})_4(8-x)\text{H}_2\text{O}\) where \(x>1.4\). It is formed by oxidation of vivianite. The precise oxidation limits between which the triclinic lattice is stable are not known, but the structure persists close to total oxidation of all iron [Rodgers 1986].

24 Santabarbaraite, an X-ray amorphous iron hydroxy phosphate \(\text{Fe}^{3+}_3(\text{PO}_4)_2(\text{OH})_55\text{H}_2\text{O}\), is formed by oxidation of vivianite. It has been reported as a yellow-brown alteration product of vivianite in lake sediments; the altered vivianite concretions displayed a yellow to brownish rim, surrounding the blue center of vivianite, which is amorphous and seems to correspond to santabarbaraite [Pratesi et al. 2003; Fagel et al. 2005].

Fig. 2.11  Detail of Gerard van Honthorst, *Frederik Hendrik’s Steadfastness*, 1650-52, Oranjezaal, No. 17. The black hair of the triton shows whitened areas as a result of bone black degradation. Photo: SRAL.

Fig. 2.12  Jacob van Campen, *Part of the Triumphal Procession with Gifts from East and West*, 1651, Oranjezaal No. 30. Detail of yellow fruit showing a gritty surface texture as a result of metal soap aggregate formation in the lead-tin yellow paint. Photo (painting): Royal Collections.
source near Haarlem, where both De Grebber and De Bray lived. The term ‘Harlems Oltramarin’ is recorded by Richard Symonds in his notebooks of the 1650s [Spring 2003]. It is also listed as ‘Haeerlaems oltomarijn’ in the inventory from Trijntge Pieters (Rotterdam 1648), and as ‘Harlem ultramarine’ in the treatise by Edward Norgate *Miniatura, the Art of Limning* (1648-49) [Richter 2007]. Furthermore, Richter notes that the term ‘terra de Harlem’, that also quite likely refers to vivianite, is described in the manuscript *Ms. Add. 12461* (British Library 1653-1657).
However, more local sources were available in seventeenth-century Holland, e.g. in Dordrecht, as is suggested elsewhere [Spring 2003; Richter 2007]. Since all vivianite paints in the Oranjezaal have degraded, it is inferred that the deterioration is primarily caused by the inferior quality of the Dutch pigment.

Bone Black

Degradation of black paints in the Oranjezaal is essentially associated with the use of bone black, a black pigment made from the charred bones of animals. Analytically, bone black can be easily distinguished from other carbon black by its high percentage of hydroxyapatite (calcium phosphate, the principal mineral component in bone). Whitish spots were observed in the dark paint of no fewer than seven paintings by Soutman, Van Honthorst, Coques, Van Campen, and Jordaens (an area painted by Van Honthorst) (Nos. 17, 18, 19, 21, 27, 30 and 32). As a result, areas originally intended as black and dark brown – hair, eyes, shadows – have dramatically changed in appearance (Fig. 2.11). Cross-section analyses revealed that part of the bone black particles have lost their color and now appear whitish. Another significant feature, evident from the EDX analyses, is the adsorption of lead and manganese (as salts/soaps?), originating from pigment particles present in the black layer or the underlying lead white-containing ground, by the porous bone black particles. Therefore, it is proposed that the carbonized organic matter in bone black responsible for the black color has reacted away in the presence of lead [Van Loon and Boon 2004 and 2005]. The conditions under which the bone was made influenced the stability of the pigment. The X-ray diffraction pattern for the bone black samples revealed an amorphous or poorly crystalline hydroxyapatite indicating that the bone black was prepared at relatively low temperature. This suggests a poor quality bone black or the intentional use of bone brown, formed by incomplete carbonization.
The potential instability of bone black has not been considered/questioned before in oil painting. Moreover, in the primary sources of the time, the occurrence of whitish hazes on black paints was frequently mentioned in connection with lamp black (a smoke black), but hardly anything is written about color changes in bone black; bone black is even suggested as an alternative for lamp black [Van de Graaf 1958: 61-62]. However, there is a short mention on the ‘dying’ of bone black by Simon Eikelenberg in his notes on painting from 1700: ‘…the paintings by Jan Maat are not very much appreciated by the Amsterdam people because they say that the bone black he uses in his paintings dies…’ (original quote: ‘…de schilderijen van Jan Maat worden niet zo hoog geacht als voor deze bij d’amsterdammers omdat zij zeggen dat het beenzwart, ’t welk hij in zijn waar gebruikt, versterft…’) [Eikelenberg 1700: 245].

The whitening of bone black paints on two paintings by De Grebber, although optically similar to the whitening phenomenon of bone black pigment described above, turned out, after chemical analysis, to have different causes. The dark hair of a cherub in the painted vault by De Grebber (No. 22) is affected by efflorescence: FTIR imaging and SEM-EDX analysis demonstrated that lead soaps formed in the lead white-containing underlying layer migrated to the black upper layer and deposited at and near the surface, but the bone black itself stayed intact here. In a pair of dark-brown boots in another painting by De Grebber (No. 24), the whitening is caused by the presence of a degraded chalk-rich glaze layer that is applied over a dark-brown underpaint (Fig. 2.3). The chalk may point to a residual substrate of a now-deteriorated organic lake pigment, a schiet-yellow or redwood lake. Degradation of the calcium-rich surface layer also involves physical break-up at the surface inducing light-scattering, as well as the formation of calcium oxalate and lead chloride. Both degradation products contribute to the whitening effect observed at the surface. The bone black present in the dark brown underpaint is not affected. The whitening of bone black and the formation of white deposits on dark oil paint films will be explored in detail in Chapter 3 and 4.

**Lead-tin yellow**

In the study of the degradation of lead-tin yellow paints, the large availability of comparable sample material was particularly helpful in distinguishing between degradation products and impurities in the pigment. Most lead-tin yellow paints, used in yellow textile, fruit or highlights, appeared to be full of small translucent white globules that gave the paint surfaces a pronounced gritty texture (Fig. 2.12). These translucent lumps were found to be (mineralized) lead soap aggregates as shown by FTIR imaging,

---

27 This citation was drawn to the authors’ attention by Margriet van Eikema Hommes.

28 In a jacket of an old man in a painting by De Bray (No. 26), a similar surface degradation was observed. Here as well, the surface layer applied over a dark underpaint contained pure chalk. This example will also be discussed in more detail in Chapter 4 on white deposits on dark oil paint films.

29 FTIR absorption bands at c. 1634 cm⁻¹ (asymmetric carboxylate) and c. 1318 cm⁻¹ (symmetric carboxylate).

30 The SEM backscatter images revealed some highly scattering and amorphous regions at the surface. EDX detected lead and chloride (ratio 1:2) in these areas.

31 Lead-tin yellow was used pure, or mixed with some lead white or chalk (in the highlight of the yellow dress in one of the De Grebber’s *Triumphal Processions* No. 28).
Chapter 2

Fig. 2.15 Jan Lievens, *The Five Muses*, 1650, Oranjezaal No. 3. Overall, and light microscopic and SEM backscatter images of a paint cross-section from the red drapery showing an enormous whitish-translucent lead soap aggregate in the red underpaint containing vermilion and red lead (right). Photo (painting): Royal Collections.

Fig. 2.16 Details of the red drapery in Fig. 2.15 showing lead soap aggregates protruding through the paint surface. Photos: SRAL.
Fig. 2.17 Christiaan van Couwenbergh, *Minerva and Hercules Opening the Doors for Victory*, 1651, Oranjezaal No. 34. Overall, and light microscopic images of paint cross-section from the white speckles in the pinkish red lead-containing paint showing partly mineralized lead soap aggregates (right). Photo (painting): Royal Collections.

Fig. 2.18 Detail of the white speckles in the pinkish paint in Fig. 2.17. Photo: SRAL.
Raman and SEM-EDX analysis (Figs. 2.13 and 2.15).\(^\text{32}\) This appears to be a typical paint defect in lead-tin yellow paints [Noble et al. 2002; Higgitt et al. 2003; Keune 2005a].\(^\text{33}\) As proposed by Boon et al., the soap masses are formed by reaction of fatty acids released during drying/ageing of the paint with the excess lead oxide in the original lead-tin yellow pigment [Boon et al. 2004]. This hypothesis was further supported by the Raman measurements that were carried out on several cross-sections (Fig. 2.15). The lead-tin yellow pigment was identified as type I, \textit{i.e.} lead-tin oxide or lead ortho-stannate (Pb\(_2\)SnO\(_4\)). The Raman spectra also gave an indication of some massicot / lead oxide (PbO).\(^\text{34}\) The yellow pigment appears to be, in fact, a mixed phase of lead-tin oxide with lead oxide. Lead-tin yellow type I is prepared by heating a mixture of three parts lead oxide (PbO, PbO\(_2\), or Pb\(_3\)O\(_4\)) and one part tin oxide (SnO\(_2\)) at temperatures between 650 and 800 °C. Several varieties of lead-tin yellow were available at that time, probably made by heating at a lower or higher temperature. Lower temperatures yield a more orange color, and higher temperatures yield more lemon-hued colors [Eastaugh 1988]. The choice to make a lighter or darker product was thus intentional to some extent. This implies that its manufacture was variable in the seventeenth century resulting in variable, inhomogeneous end products of lighter or darker yellow. It was the artist’s choice whether he wanted to use a lighter or darker product.

In some samples, the surrounding lead-tin yellow pigment has reacted away, leaving white tin oxide residues. Tin oxides nearby protrusions have been reported before and were at the time interpreted as deterioration products [Higgitt et al. 2003]. Interestingly, in nine different cross-sections of pure lead-tin yellow paints and mixed greens from the Oranjezaal, similar clusters of tin oxide, ranging between 1 \(\mu\)m and 3 \(\mu\)m across, were detected by SEM-EDX inside intact pigment lumps (Fig. 2.14). This suggests that the tin oxide is not a degradation product, but is instead unreacted tin oxide from the production process. To get a complete conversion of the starting reagents, the conditions in the melt (temperature and stoichiometry) play a crucial role. At too high a temperature, phase separation can occur with re-formation of some tin oxide [Eastaugh 1988]. Alternatively, tin oxide may have been introduced after the cooling down process, to make the color intentionally lighter. It is typically white to off-white in color. Tin oxide as a deliberate addition to the pigment during manufacture is also

\(^{32}\) FTIR imaging showed a strong absorption band at \(c.1510-20\) \(\text{cm}^{-1}\) characteristic of the lead carboxylate group \(\nu\) (COO). Many of the aggregates also contained lead carbonate as seen by a strong FTIR band at \(c.1400\) \(\text{cm}^{-1}\), assigned to the carbonate group, and a strong Raman band at 1052 \(\text{cm}^{-1}\) from (basic) lead carbonate. Mineralization of the lead soaps to (basic) lead carbonate probably takes place as a result of a reaction with CO\(_2\) that has diffused into the paint from the air. SEM-EDX analysis gave detailed information on the morphology of the aggregates, and confirmed the lead involved in the soap formation. The high-resolution backscatter images show the precipitation bands associated with mineralization.

\(^{33}\) In the Oranjezaal, aggregates were only found in lead-tin yellow and red paints, and not in pure lead white paints, illustrating the lower reactivity of lead carbonate and/or lesser oil absorption by this pigment under comparable environmental conditions.

\(^{34}\) Raman microscopy was carried out at the Scientific Department of the Metropolitan Museum, November 2006. The Raman spectra were recorded with a Renishaw System 1000 spectrometer using a laser with \(\lambda=785\) nm. Measurements of cross-sections HTBS 30x21 (yellow fruit No. 30) and HTBS 28:2001x12 (yellow dress No. 28) showed Raman bands at \(c.457\) \(\text{cm}^{-1}\) (m) and \(c.525\) \(\text{cm}^{-1}\) (w) characteristic of lead-tin yellow type I, as well as a Raman shift at \(c.289\) \(\text{cm}^{-1}\) (s) attributable to massicot (lead(II) oxide) [Bell et al. 1997].
mentioned in the literature [Burmester and Krekel 2000]. Potters have used tin oxide as an opacifier in ceramic glazes for hundreds of years. As noted by De Mayerne, some painters like Van Dyck experimented with tin white in oil paint in the seventeenth century, but it has yet to be identified in any of his paintings [De Mayerne recipe 33, 41 and 41a, Van de Graaf 1958: 35, 151, 152, 164, 165; Kirby 1999; Roy 1999].\(^{35}\) In any case, the detection of tin oxide clusters in the lead-tin yellow pigment illustrates once more the heterogeneous composition of the pigment due to variations in the manufacturing process.

**Vermilion / Red Lead**

Expensive pigments, such as lead white or red vermilion, were regularly adulterated with cheaper but visually comparable pigments.\(^{36}\) Lead white adulterated/mixed with chalk was known under the name *lootwit* in the seventeenth century [Van de Graaf 1959: 34-35]. These impurities can significantly reduce the paint’s durability, which is clearly demonstrated in some red paint layers where the formation of protrusions seems to originate from red lead (\(\text{Pb}_3\text{O}_4\)) added as a cheap adulterant to the relatively expensive vermilion.\(^{37}\) The surface of the red cloth in *The Five Muses* by Lievens (No. 3) is covered with crater-like holes filled with whitish material (Figs. 2.15 and 2.16). These are the result of the formation of metal soap aggregates protruding through the paint surface. A cross-section of a crater-like structure demonstrates a white translucent mass measuring 300 \(\mu\text{m}\) across (Fig. 2.15). The SEM backscatter image reveals a scattering solid mass where the lead soaps have mineralized, most likely into (basic) lead carbonate. EDX detects lead and carbon in the mass. The pustule appears to originate from a red underlayer, containing vermilion and red lead, which also demonstrates smaller lead soap aggregates ranging between 10 \(\mu\text{m}\) and 50 \(\mu\text{m}\) across. Although it can be argued that red lead was deliberately added to the paint as a siccative - to improve the drying process since vermilion has poor drying properties - the large quantity of red lead present in this paint layer makes it more likely that we are dealing here with an adulterated vermilion. This is further supported by the numerous warnings in the historical treatises against the use of pre-ground or ready-made vermilion, as it was often adulterated with red lead, which demonstrates that this was indeed common practice in the seventeenth century [Van de Graaf 1958: 54; Van Eikema Hommes 2004: 30].

Protruding soap masses in surface layers in other paintings also appear to be associated with the use of red lead. The formation of these soap masses not only causes a change in texture, but can also affect the color when the soaps mineralize to white opaque (basic) lead carbonate by reaction with atmospheric carbon dioxide (\(\text{CO}_2\)). It has also been found that red lead can directly convert to (basic) lead carbonate in the

\(^{35}\) However, it was probably not much used in oil: it is quite unsuitable as the color would not be very white; it has a low refractive index and it tends to be hygroscopic. Information provided by Jo Kirby 2007.

\(^{36}\) Economical use of vermilion is also reflected in the layer build-up. There are numerous examples of red-colored areas in the paintings of the Oranjezaal that are underpainted with a red earth and where the relatively expensive pigments vermilion and cochenille are restricted to the upper paint layers.

\(^{37}\) It must be noted, however, that vermilion used in a surface paint is less likely to go black if red lead is present [Spring and Grout 2002: 57]. See also the sub-section on glazing of vermilion paints.
presence of CO₂ and moisture, causing an overall lightening of the red-lead containing paint film [Saunders et al. 2002]. In paintings by Van Honthorst (No. 17) and Van Couwenbergh (No. 43), orangey highlights that consist of pure red lead applied on red paints appear to be full of lead soap aggregates, demonstrating the strong reactivity of red lead with fatty acids from the oil. The upper portions of these surface layers have clearly mineralized to (basic) lead carbonate, and, in addition, appear cracked because of
the volume changes and low flexibility of these carbonate lumps. Furthermore, the white dots/speckles in the pinkish paint on the doors painted by Van Couwenbergh (No. 34) also originate from red lead that has converted to lead soap/carbonate masses (Figs. 2.17 and 2.18). Here, Raman measurements of a cross-section collected from the pinkish paint confirmed the original red lead pigment, and, in addition, detected (basic) lead
carbonate and a small amount of lead soaps in the white masses/inclusions responsible for the white spots observed at the paint surface (Fig. 2.19).  

Verdigris / blue verditer

Verdigris, a blue/green synthetic copper acetate, was not identified in the Oranjezaal paintings. This appears to correspond with the written contemporary sources, which indicate that verdigris was less frequently used in the mid-seventeenth century, especially in landscape paintings, partly because of its potential discoloration from blue/green to brownish tones [Van Eikema Hommes 2004: 78-80]. Its dominant color must have been another reason for its declined popularity causing painters to look for alternatives. Apparently they found a good substitute in blue verditer, a synthetic basic copper carbonate ($2\text{CuCO}_3\cdot\text{Cu(OH)}_2$), which was used relatively often in green areas in the Oranjezaal paintings (Coques, Jordaens, Van Campen, Van Everdingen, Willeboirts Boschaert, De Grebber, De Bray, Van Couwenbergh). Blue verditer has the same composition as azurite, the naturally occurring mineral, but shows a distinct particle morphology. The pigment appears as small spherical greenish-blue particles with lobed outlines often with a central dark spot (like a rosette or donut), as opposed to the angular and often coarse azurite particles. The backscattered electron image displayed in Fig. 2.20 clearly shows the typical blue verditer spherulites in a green paint from Jordaens’ Frederik Hendrik in Triumph (No. 32). The small particle size of a few

---

38 The Raman spectra were recorded with a Renishaw System 1000 spectrometer using a laser with $\lambda = 785$ nm. The red lead pigment shows strong Raman features: a strong band at 549 cm$^{-1}$, and weak to medium bands at 311 cm$^{-1}$ and 391 cm$^{-1}$ that closely correlate to reference data [Bell et al. 1997]. The white inclusions show a strong band at 1052 cm$^{-1}$ assigned to (basic) lead carbonate.
micrometers across and the absence of trace elements easily distinguish the pigment from the green spherical malachite of a naturally precipitated source, which was recently found in early German and Italian paintings [Heydenreich et al. 2005]. EDX analysis detected copper, carbon and a strong oxygen peak. The presence of a carbonate group was also confirmed using specular reflection FTIR imaging (Fig. 2.21). It was difficult, however, to determine the exact color of the particles and, therefore, to distinguish between a possible blue or green verditer when examining the cross-sections with the light microscope, especially since the fine particles were embedded in a yellow/brown matrix that obscured their color. Instead, Raman was more effective in identifying blue verditer in several cross-sections (Fig. 2.22). Blue verditer and azurite yield the same/identical spectra, which are different from green copper carbonates.

There were no apparent signs of degradation associated with the use of this synthetic spherical copper pigment. Copper carbonates are less reactive to the oil medium compared to copper acetates [Gunn et al. 2002], and some yellowing or darkening of the medium enhanced by the copper pigment does not disturb an intended green tone as much as an intended blue. It was notable in the Oranjezaal paintings that blue verditer could produce a very strong green color. The green color is well preserved in most of the green draperies/textiles where the pure pigment was more often used with small additions of chalk/yellow lake. Verditer was also mixed with a range of other pigments (chalk/yellow lakes, lead-tin yellow, smalt, lead white, carbon black and/or fine red earth) to produce a variety of green tones for the foliage. It was not used in blue tones. Degradation as observed in some green glazes can be ascribed to the presence of other unstable pigments (yellow lake, lead-containing pigments or smalt) that change the paint matrix surrounding the sometimes sparsely distributed blue copper particles, making it more transparent and browner/darker, rather than deterioration of the copper pigment itself.

39 Naturally formed spherical malachite also contains silicates, potassium aluminum silicate and sometimes dolomite, but these were not detected in our samples by SEM-EDX.
40 Strong FTIR absorptions at c.1415 cm⁻¹ and c.1490 cm⁻¹ from the carbonate group.
41 Blue and green verditers (ashes) were originally prepared from the copper nitrate solution remaining from the refining of silver. The technology by which they were manufactured appears not to have been well understood in the seventeenth century, resulting in variable products [Kirby 1999]. The product was only sometimes blue, and, more often, the less valuable green. It was also suggested to wash the product with smalt to obtain the blue ashes. Research by Peter Mactaggart has shown that the color of the product depends on the temperature at which the reaction was carried out and how much the solution is stirred. Green verditer is produced when blue verditer is made at slightly too high temperature [Mactaggart 1980]. This variety in color makes it even more difficult to make a clear distinction between blue and green verditer.
42 The Raman spectra were recorded with a Renishaw System 1000 spectrometer using a laser with λ= 514 nm. The dense areas in the cross-sections, where the particles were exposed to the surface and appeared more bluish, yielded good Raman signals. We measured a cross-section from the green garment of Hymeneus in Jordaeins’ Frederik Hendrik in Triumph (No. 32), sample HTBS 32x35b, and one from a green area in Coques’ Frederik Hendrik Receiving Survivance for Willem II (No. 19), sample HTBS 19x21. They showed strong bands at c.403 cm⁻¹ that corresponded to the spectrum recorded of a blue verditer reference sample provided by the English Heritage, UK.
43 X-ray diffraction powder data are also found to be the same for blue verditer as for azurite [Gettens and West Fitzhugh 1993, pp. 31].
Fig. 2.25 Theodoor van Thulden, *Part of the Triumphal Procession with Elephant and Paintings*, 1651, Oranjezaal No. 29. The green color of the leaves is preserved in the part covered by the frame. Light microscopic image of the cross-section from the preserved green showing a yellow-green upper layer containing vivianite and yellow lake (right). Photo (painting): Royal Collections. Photo (detail): SRAL.

Fig. 2.26 Gonzales Coques, *Frederik Hendrik Receiving Survivance for Willem II*, c.1650, Oranjezaal No. 19. Strewn azurite is used in the blue sash of Hollandia (woman at the left) to preserve the blue color (lower left). The SEM backscatter image of the cross-section shows that the azurite particles (outlined in red) at the surface are embedded in the smalt layer below (lower right). Photo (painting): Royal Collections. Photo (detail): SRAL.
Fig. 2.27 Jacob Jordaens, *Allegory on Time*, 1650, Oranjezaal No. 33. Overall and details of degraded, cracked blue drapery with cross-section images showing smalt underpaint and ultramarine upper layer. Photo (painting): Royal Collections. Photo (details): SRAL.
RED AND YELLOW LAKES

Already in the seventeenth century it was known that the red and yellow lake pigments were prone to discoloration. The sources contain numerous warnings about not exposing them to the sun [Van Eikema Hommes 2004]. Lake pigments are prepared by the precipitation or adsorption of an organic dyestuff, extracted from various plants or insects, onto an insoluble/inert inorganic substrate, usually alumina or a mixture of alumina and chalk. The red and yellow colorants generally possess poor light-fastness properties, making them particularly susceptible to photochemical degradation with color loss/fading as consequence. The exact mechanisms have not been characterized yet. However, the colorfastness of the lakes can strongly vary, depending on the type of dye and its complexation with the substrate. Cochineal and madder lakes are reasonably light-fast, while the redwood lakes, like brazilwood, and most yellow lakes, derived from weld, buckthorn berries or yellow dyewoods, are extremely vulnerable to degradation.

In addition, dyestuffs precipitated on chalk are considered less stable than those on aluminum-containing substrates [Saunders and Kirby 1994a]. The use of chalk or other varieties of calcium carbonate as substrate was more often found in recipes for the inferior lake pigments, the yellow lakes, as well as the red lakes from redwoods.

In the Oranjezaal paintings, red lake pigments were particularly commonly used for the draperies, flowers and flesh tones, mixed with lead white and pure in translucent glazes. It is notable that most red glazes are well preserved showing no significant color loss. A survey of the red glazes to characterize the dye components was carried out using HPLC [Clarke et al. 2003]. They were found to consist mostly of (Mexican) cochineal, occasionally mixed with brazilwood or weld; one pure brazilwood was identified in the shadow area of the red clothing of Frederik Hendrik in Van Thulden’s *The Education of Frederik Hendrik* (No. 10) and one brazilwood with a trace of cochineal in the palette in Soutman’s *Allegory on the Excellent Rule of Frederik Hendrik* (No. 15). The results seem to accord with contemporary sources that recommended cochineal for high-quality work. Furthermore, the substrates were characterized as amorphous aluminum hydroxide using TEM [Clarke et al. 2003].

In two glaze layers in the shadow areas of red clothing that now appear grayed and degraded, the presence of a deteriorated red dyestuff was suspected but was not identified with HPLC. In *Triumphal Procession with Spoils of War* by De Grebber (No. 24), the boy at the far right wears a red coat. Stylistically, it seems likely that originally a red or red-brown glaze was used for final modeling of the shadows, applied over the red-brown underpaint layer containing red earth and carbon black. SEM-EDX analysis of the surface glaze layer(s) demonstrated the presence of fine red earth and particles of calcium sulfate and calcium carbonate, possible residual substrates of now-faded red lake pigments. A substantial amount of calcium sulfate was also detected in the surface glaze.

[44] The presence of ellagic acid in the cochineal/brazilwood mixtures in samples HTBS 11A1 (Willeboirts Boschaert) and HTBS 3A2 (Lievens), as detected by HPLC, suggest a textile origin for these lakes: the dyestuffs were recycled from clippings or ‘shearings’ of dyed cloth. Ellagic acid, i.e. tannin, in a textile could be due to ‘weighting’ of silk with galls, or could have acted as an additional mordant. It could also be due to a black dye, but a black-dyed textile would not be used for preparing red lake [Clarke et al. 2003].
of the shadows of the folds of the red clothing (of the child) in the lower right of De Bray’s *Triumphal Procession with Musicians* using FTIR imaging and SEM-EDX analysis (Figs. 2.23 and 2.24). This layer further contained a little red earth and carbon black. In any case, the presence of calcium salts in these originally red glaze layers point to more vulnerable, inferior red lake pigments, compared to the alumina-substrated cochineal lakes discussed above.

The same difference can be found with yellow lakes: the chalk-based yellow lakes or *schiet*-yellows were considered inferior even to yellow lakes complexed with alumina. In mixed greens with blue verditer or vivianite, additions of chalk were found that suggested the presence of degraded yellow lakes added to the blue pigments to obtain a green tint. In most cases, however, it was not possible to identify the dyestuffs since they were usually highly degraded showing nothing detectable by HPLC. We were only successful in one case where the paint had been shaded from the light by the frame rebate: weld, a flavonoid yellow dye, was identified in a green leaf in Van Thulden’s *Triumphal Procession with Elephant and Paintings* (No. 29) from an area protected by the frame (Fig. 2.25). Degradation of the yellow lakes not only resulted in fading, giving the green foliage a more bluish tone than originally intended, but also gave the paint a blanched/grayish appearance.

The chalk in the degraded glaze layer applied over the dark-brown underpaint in the leather boots in De Grebber’s *Triumphal Procession with Spoils of War* (No. 24), as discussed in the bone black section, may also point to a residual substrate of a now-deteriorated organic lake pigment. Degraded chalk-rich glaze layers will be further discussed in Chapter 4.

**Influence of Binding Medium on Preservation**

In the seventeenth century, artists primarily used oil binders (poly-unsaturated triglycerides) that chemically dry by a process of oxidative polymerization to form a hard, durable film [Van den Berg 2002]. These oxidation processes continue during ageing, resulting in the formation of low molecular weight breakdown products. At the same time, hydrolysis of the ester bonds of the cross-linked triglycerides takes place, which leads to the formation of free fatty acids. These are partly stabilized by their strong interaction with certain pigments. As a result of these ageing processes, the optical (color, transparency, saturation) and physical (hardness, flexibility) properties of the paint alter. The paint film may yellow or darken, become more brittle or lose its binding properties in the extreme case.

Artists modified the properties of the oil, such as the thickness and color. They heated the oil and/or added driers to improve the drying process. In addition,
some pigments, such as lead white or red lead, were known to be good driers and to form more durable films due to their strong pigment-medium interaction, whereas others tended to inhibit the drying process of the oil, e.g. the carbon-based blacks and lake pigments. They also tried to bleach the oil in the sun to obtain a lighter color. Sometimes small amounts of other media were added to the oil, such as resin, protein or gum, to further manipulate the handling and optical properties. Apart from manipulation of the medium itself, they made use of certain pigment-oil combinations to obtain translucent paints or impasto effects [White and Higgitt 2006]. It is also known from instructions in the contemporary artists’ manuals that artists were aware of the problem of yellowing of the oil medium, and tried to combat the yellowing with different methods, such as washing the oil or using another medium that was less prone
Fig. 2.30 Detail of Jacob van Campen, *Part of the Triumphant Procession with Gifts from East and West*, 1651, Oranjezaal No. 30, showing degraded blue skirt. Cross-sections (BF and UV) from light blue area (*upper row*) reveal ultramarine mixed with lead white; cross-sections (BF and UV) from discolored shadow area (*lower row*) reveal a thin, almost pure ultramarine glaze over a vivianite-containing underpaint layer.
to yellowing [Van Eikema Hommes 2004: 18-27]. However, it remains questionable to what extent these instructions were followed in practice, especially since some of these methods are difficult to prove analytically. In this section, we will study how the painter’s choice and treatment/modification of the medium relates to the state of preservation and appearance of the paint.

**Oxidation State of the Binding Media**

The Oranjezaal presented a unique opportunity for a comparative study of the binding medium composition of samples from different paintings. Py-TMAH-GCMS of white and dark samples from a selection of paintings revealed that linseed oil was the main binding medium used [Ferreira et al. 2005]. Little evidence was found of the use of heat-bodied or stand oil, but rather of the addition of driers or pigments with good drying properties (lead driers and umber) in paints containing pigments with poor drying or antioxidant properties, such as carbon and bone blacks. Although all the paintings studied have a common history, a significant variation in the degree of oxidation, degree of drying and detailed chemical composition of the binding medium was still found. There are differences in the way lead white and dark pigments influence the final composition of the binding medium. In general, lead white-containing paints showed a higher degree of oxidation (detectable by the higher relative amounts of certain compounds including diacids), whereas some examples of the dark paints showed evidence of poor drying properties (e.g. the presence of unsaturated fatty acids). Due to the nature of this set of samples, it can be concluded that the chemical differences of the oil medium are mainly a result of interactions of the medium with pigments and other additives, although the differences in the degree of light exposure cannot be entirely ignored. Therefore, it is possible to relate them to the combination of materials used to prepare the paint.

**Prevention of Yellowing of the Binding Medium**

Linseed oil was commonly used as a binder in seventeenth-century painting practice, even though it has the tendency to turn yellow over time. The optical effect of this yellowing is most disturbing for white and blue paints; it spoils the clarity of the white and gives the blue a green hue. Although seventeenth-century painter’s manuals recommend the use of media that are less prone to yellow, for example walnut or poppy

---

47 This binding medium survey was started by Gisela van der Doelen and completed by Ester Ferreira.
48 Painters manipulated the working properties of the oil, viscosity, drying time, by heating the oil, often in combination with siccatives. During heating, isomerisation of the double bonds takes place, which leads to dicarboxylic acids other than azelaic acid (C9 diacid). The amount of azelaic acid, relative to the other dicarboxylic acids is high for films of cold-pressed linseed oil, and low for heat-bodied linseed oil films. The identification of heat-treated oil is based on the ratio between azelaic acid and suberic acid (C8 diacid) [Mills and White 1982]. The Gaussian distribution of diacids of C6 to C12 is another typical feature of strongly prepolymerized oils. See also review in PhD thesis by Van den Berg [Van den Berg 2002].
49 The light conditions are not completely uniform throughout the hall due to exposure to daylight from the windows and the cupola. Some paintings are directly lit by the sun whereas others are in relatively dark areas of the hall. In addition, the position of the sun changes during the day and with the seasons. During the last restoration, the windows were fitted with UV protection and sun blinds.
The relationship between preservation and technique in the paintings of the Oranjezaal

oils for white paints and also water-based binding media for blue paints [Van Eikema Hommes 2004, pp. 20-22], this was more the exception than the rule in the Oranjezaal. The results suggest the use of walnut oil or a mixture of drying oils in the white paints in only 4 of the 15 white paints analyzed.\(^50\) It is likely that artists also used other methods to process the oil in an attempt to obtain more permanent colors, such as washing the oil or exposing it to the sun. In the historical treatises, there are numerous hints that painters tried to oxidize and bleach the oil by exposing it to the air and sunlight [Keller 1973]. The result was a thickened oil medium with a much lighter color. Unfortunately, it is not possible to discern sun-thickened oil analytically from unmodified (linseed) oil, since the process is comparable with the normal drying process in the light (photo-oxidation).

In a few blue paints, we found good indications for the use of a water-based medium, as the only medium or as additive to the oil, or another application method to overcome/combat the yellowing/darkening of the medium. For ultramarine, a small percentage of egg yolk was detected, besides oil, in the upper paint layer of the blue drapery in Jordaens’ Allegory on Time (No. 33) using a combination of FTIR and GC-MS analysis.\(^51\) The ultramarine paint has retained its blue color despite the drying problems in the paint structure (see also the sub-section on blue draperies). Furthermore, the bright blue petals in Soutman’s Triumphal Procession with Prize Gold and Silver (No. 27) were found to contain azurite bound in starch, the grains of which were observed under the polarizing microscope\(^52\); the detection of the polysaccharides using DTMS confirmed this identification.\(^53\) Moreover, Coques seems to have used azurite without a binder in the blue sash of Hollandia (No. 19), applied as dry powder on top of the wet paint to ensure it retained its desired color. The backscattered electron image displayed in Fig. 2.26 clearly shows coarse azurite particles at the paint surface embedded in the underlying paint, which is a mixture of smalt and lead white. This technique may have been copied from the practice of strewing smalt [Dynasties 1995] and is also mentioned by De Mayerne [Van de Graaf 1958, recipe 49a]. Van Couwenbergh’s Herald (No. 43) is also noteworthy, where the now dark-green appearance of the blue clothing was indeed caused by a darkened medium. However, the binding medium of the azurite paint in

---

\(^50\) The P:S ratio is between 2 and 2.5 in samples from Nos. 2 (top side of the wheel of the carriage) and 19 (white feather on the hat). One sample from No. 19 (white highlight on the dress) has higher P:S ratio of 4, which suggests the use of walnut oil, poppy oil or a mixture of drying oils. The ratio of the molecular ions of the palmitic and stearic acids (P:S) is considered to be a relatively stable feature and thus is commonly used to identify the type of drying oil [Mills and White 1994]. A drying oil with P:S less than 2 can be identified as linseed oil, and P:S greater than 5 as poppy oil. Intermediate ratios can be assigned to walnut, poppy oil or mixtures of these with linseed oil. These results should be interpreted with caution, since migration of fatty acids between paint layers may alter the P:S ratios in individual layers.

\(^51\) GC-MS analysis was carried out at the Getty Conservation Institute, Los Angeles, October 2003 by Joy Keeney and Michael Schilling.

\(^52\) PLM was carried out by Tineke Oostendorp, Oosterbeek, 2002.

\(^53\) DTMS of the blue petal (sample HTBS 27A4) shows mass peaks at m/z 60, 73, 114, 126 and 144, characteristic of hexoses.
Fig. 2.31 Detail of Pieter de Grebber, *Part of the Triumphal Procession with Sacrificial Bull*, 1650, Oranjezaal No. 28, showing the lower part of the red dress where only the final zigzag brushstrokes with pure vermilion have turned gray, with light microscopic (*upper row*) and SEM-EDX images (*middle row*) of the cross-section from a grayed brushstroke.
The relationship between preservation and technique in the paintings of the Oranjezaal

Fig. 2.33 Detail of Christiaan van Couwenbergh, *Herald (Southeast)*, 1648-1652, Oranjezaal No. 44. The yellow highlight of the red jacket of the herald has sunk, due to slow drying of the paint, which has allowed the orpiment particles (recognizable as elongated flakes in the backscatter image) to sink. Photo (painting): Royal Collections. Photo (detail): SRAL.
the herald's jacket was found to consist mostly of resin, apart from some traces of oil.\textsuperscript{54} The use of a fast-drying resin may have been dictated by Van Couwenbergh's working \textit{in situ}.\textsuperscript{55} Finally, for smalt, there was no evidence of the use of media other than oil.

\textbf{INFLUENCE OF PAINTING TECHNIQUE ON PRESERVATION}

Thus far, we discussed the relationship between the quality of the individual pigments and media and the observed paint defects, but differences in deterioration can also develop by the way in which the various materials were used and combined. The painting process is reflected in the layer build-up. We can distinguish several stages, including the sketch, the undermodeling, the working up and the final glazing and highlighting. Within these layers, artists used various pigment combinations to achieve certain illusionistic or painterly effects, while they varied in color, thickness, texture, consistency and transparency of the paint. Some combinations have proven not to stand

\textsuperscript{54} DTMS of the dark blue coat identifies a mixture of oxidized abietic acids (mass peaks at \textit{m/z} 253, 271, 301, 314, 315, 330), diterpenoid resins characteristic of pine resin. In addition, the spectrum shows traces of triterpenoid resins, aged mastic and dammar (\textit{m/z} 143, 163, 399, 414, 424, 440/442, 454, 468). However, the possibility of pine resin varnish sinking into poorly bound paint should also be considered. The paint was very sensitive to solvents during sampling. The mastic and dammar (certainly the latter) must be due to a later varnish.

\textsuperscript{55} Van Couwenbergh painted the figures of the \textit{Heralds} in the room itself and therefore may have been looking for fast working methods. The fact that one of the Heralds (No. 45) is left unfinished suggests that he was rushing at the time.
the test of time, whereas others made the paints less prone to deterioration. This section examines the way in which the layer structure (blue draperies, red lake glazing over vermilion paint, orpiment), admixtures of lead white (in vermilion, smalt, ultramarine and light-sensitive lake and earth paints), the layer thickness (indigo), mixtures of incompatible pigments (lead- and copper-containing pigments with orpiment), and the preparation of the oil (orpiment) have influenced the state of preservation of some Oranjezaal paints.

**Blue Draperies**

In the Oranjezaal paintings, the degraded appearance of the blue draperies painted with ultramarine, a complex sulfur-containing sodium aluminum silicate, appears to be mainly the result of the use of cheaper and less permanent colors in the underpainting, although ultramarine in oil is not always considered to be very stable. The term ‘ultramarine sickness’ describes a phenomenon where the ultramarine paint has lost its blue color and appears grayed/whitened at the surface. When noted on oil paintings, this discoloration is usually associated with disintegration of the binding medium, while the ultramarine particles are in good condition. This phenomenon, however, was not observed in the Oranjezaal paintings. Here, the degradation is associated with discoloration of the underlying layers. The application of successive layers of different blue pigments is partly dictated by the price. Natural ultramarine, obtained from the semi-precious stone lapis lazuli, was extremely expensive and, therefore, was often replaced by cheaper blue pigments in the underlayers.

The blue drapery of the personification of Time (as an old man) in Jordaens’ *Allegory of Time* is built up in three different blue layers. Indigo is used for the undermodeling, the drapery is further worked up with a smalt/lead white-containing paint and finished with a thin layer of ultramarine in a few brushstrokes. The successive application of smalt and ultramarine layers has locally caused severe cracking of the paint (Fig. 2.27). The smalt paint seems to have contracted in little islands, which distort the appearance of the drapery. The reason of this cracking is not entirely clear. Differences in drying time and particle size probably play a part. The rather coarse smalt is bound in oil, whereas in the fine ultramarine upper layer, some egg yolk in the binder apart from the oil was also detected (see previous section). The ultramarine paint has retained its blue color, but it must be said that the ultramarine paint has a particularly matte surface appearance and was very sensitive to exposure to solvents during cleaning. Perhaps the ultramarine finish was applied before the smalt underpaint had completely dried, and this may have caused the premature cracks, since smalt dries preferentially at the surface. Degradation of the smalt paint may also be held responsible for the cracked appearance.

---

56 Micro-fissures are observed at the paint surface that scatter the light, resulting in a whitened surface appearance [Groen 1993]. However, there are occurrences where the ultramarine itself has lost its color under acidic conditions [Plesters 1993]. This has also been observed in fresco paintings and the mechanism was recently revealed by scientists at New York University, Pratt Institute and Metropolitan Museum of Art. They discovered that the aluminosilicate framework breaks apart and releases color-forming sulfur molecules [Del Federico et al. 2006].

57 Before the nineteenth century, the only known source of lapis lazuli was in the quarries of Badakhshan (northeastern Afghanistan [Plesters 1993]).
of the blue drapery. The paint cross-sections reveal that the smalt particles are severely discolored. The deterioration of smalt is often accompanied by physical degradation of the paint film, like disintegration of the binding medium and the development of cracks [Spring et al. 2005]. Drying cracks were also observed in some sky paints that contain discolored smalt (Nos. 11, 16, 33). The cracking is particularly pronounced in areas where many layers are applied on top of each other. For example, a cross-section collected from a cracked area in the sky in Willeboirts Boschaert's *Frederik Hendrik as Lord of the Seas* (No. 16) shows four successive layers of smalt-containing paint.

Comparable to the drapery of *Time*, cross-section analysis of the blue quiver (container for carrying arrows) in Van Everdingen’s *Allegory on the Birth of Frederik Hendrik* (No. 1) reveals the application of an ultramarine finish over a smalt-rich underpainting. Here, the ultramarine layer looks very abraded and over-cleaned at the surface, primarily in the areas where it covers the smalt paint; in the areas where the ultramarine paint is applied over a different underpainting, it seems unaffected (Fig. 2.28). Where the smalt underpaint is now exposed at the paint surface as a result of abrasion of the upper layer, it appears very grayed and crusty. Also the cross-section demonstrates discolored, coarse smalt particles. Therefore, it is inferred that deterioration of the smalt paint is largely responsible for the now-degraded surface appearance and loss of modeling of the blue quiver. It seems as if it has pushed off the ultramarine layer. In addition, the ultramarine paint is probably weakly bound and very thinly applied, although there was no indication of a binding medium other than oil.58

Also, in other blue draperies, in less extreme cases, loss of modeling can be associated with the deterioration of smalt used in the undermodeling. For example, the blue dress in the *Triumphal Procession, Amalia and her Daughters observing the Victory* by Van Honthorst (No. 31) now appears rather flat (Fig. 2.29). Much of the modeling is achieved in the smalt-containing underlayer, which shimmers through the ultramarine finish. The ultramarine paint is only applied as a thin, uniform layer for the special color effect. Therefore, discoloration of the smalt paint shows through and results in loss of modeling in the dress.

As mentioned earlier, the blue skirt of a girl in Van Campen’s *Triumphal Procession* (No. 30) is undermodeled in vivianite paint, while the final layers contain ultramarine. Unfortunately, the shadow areas of the skirt have turned brownish over time resulting in loss of modeling. Here, cross-sections show a very thin ultramarine glaze without lead white (Fig. 2.29). Their brownish appearance is probably the result of the combination of a discolored underpaint containing vivianite shimmering through the thin glaze and darkening of the ultramarine layer itself. It is notable that

---

58 We sampled a highlight where the blue paint was thicker and appeared still intact. It was noticed that the paint was a little sensitive to the solvent mixture of ethanol : iso-octane used to remove the varnish prior to sampling. The binding medium was identified using both FTIR and DTMS. In addition to the normal oil components (P:S \( \approx 1 \)), DTMS detected lead azelate at \( m/z \) 348-350. FTIR also indicated the presence of lead soaps, as well as calcium oxalates (absorption bands at 1629 cm\(^{-1}\) \( \nu(COO) \) and 1326 cm\(^{-1}\) \( \nu(COO) \)). The presence of oxalates has been observed more often in ultramarine paints. They probably form by oxidative degradation of the oil medium. This might explain the reduced binding properties/physical break-up of the medium. In the intact sampled area, the paint is probably stabilized by the lead white/soaps.
the ultramarine particles themselves still appear blue in cross-section, but that the paint matrix around the particles is darkened. The presence of some lead soaps and/or calcium oxalates in the medium, as detected by DTMS, may have contributed to the darkened appearance. By contrast, the blue color is still well-preserved in the light parts of the skirt. A cross-section from this area reveals a thick upper layer of ultramarine mixed with lead white (Fig. 2.30). It is proposed that the paint film is stabilized by the lead white owing to its strong coordinating properties with the oil network (see also the sub-section on the admixture of lead white).

From the above, it is concluded that the use of smalt and vivianite in underpaint layers as substitutes of the expensive ultramarine have caused problems in the blue draperies, specifically cracking, abrasion, darkening and loss of modeling. In contrast, we observed examples of the use of azurite and indigo in the underpaint where the blue is still intact. The well-preserved blue textile in *The Five Muses* by Lievens (No. 3) is built up in successive layers of different blue paint mixtures with indigo and/or azurite, applied on a gray-blue dead-coloring with indigo. It is covered with a uniform, thin glaze of ultramarine and completed with some final bright-blue strokes of a more opaque ultramarine paint.

**Glazing of Vermilion Paints**

When exposed to light, the red pigment vermilion, mercury(I) sulfide (Hg₂S), turns black/gray at the surface. Although this only affects the upper few micrometers of the paint, the visual impact is immense (Fig. 2.31). This phenomenon has already been known for a long time, but the exact reaction mechanism has only been recently elucidated using SEM-EDX and SIMS [Keune and Boon 2005]. Vermilion is first converted into black metallic mercury Hg(0) under the influence of light. Chloride ions present as trace elements in the vermilion (0.05-1%) act as catalysts in this photo-electrochemical process. Sulfide is oxidized to sulfur dioxide, which probably escapes. The black phase will react further with chloride, probably from an external source, to form white mercury chloride products, Hg₂Cl₂ (calomel) and HgCl₂. In the Oranjezaal, blackening of vermilion was only observed in the paintings by De Grebber and Van Couwenbergh (Nos. 24, 28 and 34). These painters used pure vermilion, whereas in all the other paintings, the vermilion is protected from discoloration either by mixing it with lead white or by covering it with an organic red glaze, which filters especially that part of the light spectrum that otherwise would have induced the darkening process.

---

59 A sample from a light part of the skirt where the blue color was intact was collected for binding medium analysis. Both FTIR and DTMS identified the medium as oil. The lead white is partly saponified. FTIR also shows an absorption peak at 1318 cm⁻¹, which might be an indication of calcium oxalates (compare to footnote 58). The calcium may either derive from calcite impurities associated with ultramarine or from the ultramarine structure itself (approximate compositional formula is given as (Na,Ca)₈(AlSiO₄)₆(SO₄,S,Cl)₂).

60 See also footnote 58.

61 The use of red lake glazes over vermilion underpaint has been shown to reduce the tendency of vermilion to darken [Gettens et al. 1993]. These red colorants absorb much of the high-energy blue radiation [Saunders and Kirby 1994b] that otherwise would have induced the darkening of vermilion. The role of lead white in the protection is not completely understood. It seems that, in a similar way, red lead may protect the vermilion from deterioration [Spring and Grout 2002: 57]
Thus, the occurrence of this color change seems to relate to the painting technique - to the way in which the materials were applied. Fig. 2.31 shows a detail of the red dress in De Grebber’s *Triumphant Procession with Sacrificial Bull* (No. 28) where only the final zigzag brushstrokes, square to the direction of the fold, have turned gray, strongly disfiguring the image of the skirt. The cross-section of a gray brushstroke reveals the presence of a very thin, grayish coating at the surface of the red vermilion layer. EDX analysis detected peaks for mercury and chloride in the gray film, which demonstrates the conversion of vermilion into a mercury chloride compound. Using Raman, we were able to confirm the presence of calomel in the gray film (Fig. 2.32). The other red areas are either mixed with white (light tones) or are covered by thin red glazes in the middle tones (now partly faded), or thick red glaze layers in the shadow areas, producing a large variety of red tones and color effects. The red lake in the glaze was identified as cochineal by J. Wouters [Clarke et al. 2003]. Interestingly, the use of an underpainting painted with vermilion in rose-colored draperies was also recommended in some treatises to make the color more permanent [Van Eikema Hommes 2004: 35]. The drapery could then be worked up with light-sensitive red lake paints and glazes. The intense red color of vermilion would still glow through when the lake layers are fading. Of course, this combination of layers was also an effective way to achieve the special color effect, which may have been the predominant reason of its application.

**Admixture of Lead White**

We already noted that the presence of lead white in vermilion and ultramarine paints seems to stabilize these paints. This probably has to do with the strong coordinating properties of lead white with the oil network. Mixing with lead white also makes smalt paints less susceptible to discoloration, as already mentioned by De Mayerne [Van de Graaf 1958, recipe 35g]. Discolored, pure smalt paints look brownish, whereas smalt mixed with lead white, as used in many skies of the Oranjezaal paintings, discolors to a pale blue. The admixture of lead white to the smalt paint improves its handling properties, prevents the formation of an oilskin at the surface and fills up the pore space (between the coarse smalt particles), thus reducing the excess of oil [Van de Graaf 1958: 42-43]. Moreover, the high reflectivity of lead white makes the (partly) discolored smalt particles in the paint look bluer, albeit paler (see also Chapter 5). In addition, it is possible that lead white actually slows down the degradation process.

---

62 It is not certain if maybe a chlorine-free vermilion was available at the time and used in some cases.
63 We measured the surface of an unembedded sample (HTBS 28s19) from a grayed brushstroke using Raman microscopy. Vermilion produced a strong band at c.252 cm\(^{-1}\) and weaker features at c.282(sh) and c.343 cm\(^{-1}\). The small bands/shoulders at c.270 cm\(^{-1}\) and c.160 cm\(^{-1}\) correlate to the reference spectrum of calomel (Fluka). Calomel has also been identified by other researchers in gray/black deteriorated crusts on the surface of vermilion paints [Spring and Grout 2002; Cotte et al. 2006].
64 Another cross-section of a blackened red area from the painted doors (No. 34) was measured using SIMS, which detected various mercury chloride compounds [Keune and Boon 2005].
65 The HPLC chromatogram identifies carminic acid, which is the characteristic component of the red insect-dye cochineal (an antraquinone). SEM-EDX analysis detected aluminum, potassium and sulfur in the red lake particles, indicating that the dyestuff was precipitated on an alumina substrate.
66 It is thought that there is a competition between the formation of lead soaps and potassium soaps.
While the admixture of lead white to certain pigments seems to slow down their deterioration, in other combinations, lead white noticeably accelerates the process. For example, the light-sensitive organic pigments, such as the yellow and red lakes and the organic browns, are more vulnerable when mixed with lead white than when used pure, due to the lower pigment concentration and the light-reflective properties of the white pigment [Saunders and Kirby 1994a; Feller 1997]. Likewise, the blue dyestuff indigo fades more rapidly when mixed with higher proportions of lead white [Van Eikema Hommes 2004: 149-150]. In most of the flesh tones in the Oranjezaal, a little red lake pigment is added to obtain a pinkish color. Hence, it is assumed that many of the flesh colors now look much paler than they did originally. This was already illustrated in the example of the face of the girl in Van Thulden’s *Triumphal Procession with Elephants and Paintings* (No. 29), where in the area behind the frame, the original bright pink is preserved (Fig. 2.4) (see also the section on the effect of ageing on the overall appearance). Furthermore, the brown organic-rich pigment Kassel earth showed no sign of fading when used in almost pure form in the black dog’s leg in *Triumphal Procession with Musicians* by De Bray (No. 26)\(^67\), whereas mixed with lead white in the spandrel of *The Smithy of Vulcan* by Van Thulden (No. 5), it has visibly discolored: the paint protected by the frame has a darker and more purple appearance compared to the exposed area.

**Application of Indigo Paint**

The blue organic pigment indigo is light-sensitive and gives a pale grayish or greenish hue over time. So it was recommended at that time to restrict the use of indigo to the underpaint\(^68\), and cover it, for example, with a glaze or finish of ultramarine that would protect it from fading. From the middle of the century it was also more frequently used in surface layers [Van Eikema Hommes 2004: 133-140]. Indigo is relatively well-preserved in the surface layers of the paintings in the Oranjezaal, probably owing to the painting technique that has affected the permanence of the paint. In the blue flag on the left in De Grebber’s *Triumphal Procession with Sacrificial Bull*, the application of a thick multi-layered system of indigo paint (40-60 µm) has prevented this area from color loss (Fig. 2.8). In cross-section, a discolored top is visible (5-15 µm), but there is enough unfaded blue below to preserve the blue color [Van Eikema Hommes 2004: 150].

---

\(^67\) Kassel earth was identified by a combination of techniques. The presence of long chain saturated fatty acids and alcohols (C22-26) as well as an increased level of short chain saturated fatty acids (C7-C10) are characteristic of Kassel earth pigment [Languri 2004]. FTIR suggested the presence of aromatic compounds in the pigment composition also supporting the identification of the pigment as Kassel earth. Backscattered electron images of the pigment particles showed particular structures with plant-like morphology compatible with the fossilized plant origin of Kassel earth pigments. SEM-EDX analysis detected C, O, Ca, K, Al, Fe, Si associated with the pigment particles. This further supports the given pigment identification. A small amount of lead was found dispersed through the matrix.

\(^68\) Although indigo is easy to work with, has a high color intensity, good hiding powder and fine-grained consistency.
Chapter 2

Orpiment in Mixtures and Highlights

Christiaan van Couwenbergh is the only painter in the Oranjezaal that used the pigment orpiment, a yellow arsenic sulfide (As$_2$S$_3$). Orpiment paint was more commonly used in interior painting and for decoration of naval and freight ships at that time for the rendering of gilded metal [Tångeberg 2005]; but despite its rich color, it was not regularly used by easel painters in the seventeenth century because of its many well-known disadvantages. It is extremely toxic, has a poor drying nature, is difficult to grind, is incompatible with other pigments, has lack of body and darkens in oil. Van Couwenbergh was commissioned to paint the entrance door, the sides of the fireplace, the panels between the windows and the four Heralds that stand 7.5 meters tall (Nos. 34, 43–46). He used orpiment for the highlights on the clothing, where the other painters used lead tin yellow. He also mixed orpiment with lead and copper-containing pigments, e.g. in the foliage (No. 34) or in the underlayers, but there was no evidence of deterioration (blackening), though sources frequently mention the incompatibility of these pigments.

Van Couwenbergh’s pure orpiment highlights, however, present a serious paint defect: the paint surface is sunken in but has raised edges and also seems slightly darkened. Fig. 2.33 displays a detail of the yellow decoration on the red coat of the herald (No. 44) showing the sunken highlight. The backscattered electron images of a sample taken from this area show that the characteristically long, layered/laminated flakes of natural orpiment have slightly sunk to the bottom of the paint layer (Fig. 2.33). The orpiment particles are embedded in filler material (glass; quartz; gypsum); both FTIR and DTMS identified the binding medium as pure oil. It is thought that the orpiment particles have sunk in this way because of the slow drying of the oil. Several sources, including De Mayerne’s manuscript [Van de Graaf 1958: 185, recipe 108], mention that orpiment needs strongly drying oil, but it seems that Van Couwenbergh’s oil was insufficiently pre-polymerized, severely slowing down its drying by the antioxidant properties of the orpiment and leaving enough time for the paint particles to realign after a surface film had started to form. The layer structure of another sample, collected from the ochre-colored cuirass (breast armor) of Minerva on the entrance door (No. 34), shows that the final touches with orpiment were applied over an underpainting, containing lead white, ochre and some orpiment, that was not completely dry yet. This also suggests improper use of orpiment by Van Couwenbergh, since the historical treatises contain warnings that it was to be exclusively used for the final highlights, only to be applied after all the other paint had dried completely [De

---

69 When used in paint, the pigment particles are probably encapsulated by the binding medium, and are not in direct contact with each other.

70 Interestingly, a similar problem in the highlights has been recently encountered on a seventeenth-century ceiling with painted flower decorations in a canal house in Delft. Personal communication Edwin Verweij, Office for Architectural Paint Research and Conservation, Amsterdam, 2004.

71 Glass may have been added to improve the grinding of the orpiment [Rötter 2003].

72 P:S ratio is about 1.5, which suggests the use of linseed oil. The DTMS spectra also show As$_n$(n=1→4) and As$_n$S$_m$(n,m=1→4) clusters, the typical desorption pattern of orpiment.

73 In the sources, litharge-oil (boiled), glass, alum, zinc sulfate, oil with red lead (unboiled) were mentioned as driers for orpiment. Personal communication Lidwien Speleers.
The relationship between preservation and technique in the paintings of the Oranjezaal

Mayerne recipe 73, Van de Graaf 1958: 51, 175; Van Eikema Hommes 2004: 11, 37]. No evidence has been found of bleaching, increased transparency, extreme brittleness of the paint or for increased sensitivity to organic solvents as a result of conversion of orpiment into white arsenic oxide as mentioned elsewhere [West Fitzhugh 1997; Hendriks and Wallert 1998; Dubois et al. 2001].

CONCLUSIONS

The ageing processes described in this chapter are very similar to what is observed in seventeenth-century paintings in general, except for the whitening of bone black that has not been reported before on oil paintings. It seems unlikely though that this degradation is unique for the Oranjezaal; it must have been often overlooked in the past. We have seen that the paints, even under these mild environmental conditions, are subjected to all kinds of chemical processes that have changed the original appearance of the paintings, not only disturbing the color harmony and spatial illusion, but also affecting the surface texture and flexibility of the paint. These chemical changes can make paintings vulnerable for physical damage during restoration and transport. The excellent physical condition of the Oranjezaal ensemble and the negligible paint loss owes to the low number of interventions over the course of time and to the sound preparation of the canvases and excellent condition of the grounds.

The availability of so many comparable paints of the same age and a similar history provided a context for the interpretation of the analytical results. This made it possible to relate the degree of ageing to differences in quality of pigment and binding medium and to the working methods of the painters, to how they combined and applied their materials. Although the artists were sometimes aware of how to improve the durability of their paints74, as demonstrated by the thick application of indigo or the use of red lake glazes over vermilion underpaint, in other cases they were unaware of the colorfastness of the materials, as must be the case for vivianite or bone black. Furthermore, certain color changes only became apparent after a longer time period. Some examples clearly show that the durability was not (always) their main concern, as demonstrated by the abundant use of smalt, schiet-yellow and red lakes in the ensemble, even though historic treatises show that they were regarded as problematic. In these cases, economical and availability reasons must have prevailed. They used the problematic smalt under ultramarine, since ultramarine was too expensive to use exclusively. They might also have aimed for a certain optical effect, which is probably the reason behind the use of the yellow and red lakes in translucent glazings. Therefore, we have to conclude that the choice of materials was not only dictated by their durability, but equally by their availability, price and the painterly effects the artist tried to achieve.

74 This is also shown by the numerous historical texts that contain instructions for preserving the original appearance of the paintings [Van Eikema Hommes 2004: 17-50].
ACKNOWLEDGEMENTS

The restoration was initiated by the State Building Agency (Rijksgebouwendienst (Rgd), The Hague) and carried out between 1998-2001 by a large team of conservators under the supervision of Anne van Grevenstein, Limburg Conservation Institute (SRAL) Maastricht. Technical studies of the paintings of the Oranjezaal ensemble started under the MOLART Research Program (1998-2002), and were continued in the De Mayerne Programs ‘MOLMAP’ (2002-2006) and ‘Comparative studies of paintings in the Oranjezaal’ (2002-2004). I would like to acknowledge Lidwien Speleers and Ester Ferreira who both contributed to much of the work presented in this chapter. Many thanks also to Silvia Centeno, Scientific Department, Metropolitan Museum of Art New York, for the opportunity to perform the Raman measurements with her. A book is being prepared on the Oranjezaal, edited by Rudi Ekkart, Netherlands Institute for Art History (RKD), The Hague, in which the results of the restoration and of the MOLART and De Mayerne projects will be presented (due 2009).

REFERENCES


Eikelenberg, S., 1679-1738, Aantekeningen over Schilderkunst, Regionaal Archief Alkmaar MS acquisitions collection nos. 390-394.


Van de Graaf, J.A., 1958, Het Mayerne manuscript als bron voor de schildertechniek van de barok, PhD dissertation University of Utrecht, Mijdrecht.


Keune, K., 2005a, ‘Metal soap aggregates in oil paintings from the 15th-20th century’, in *Binding medium, pigments and metal soaps characterized and localized in paint cross-sections*, PhD dissertation University of Amsterdam, Molart Series (11), AMOLF, Amsterdam, pp. 128-132.


The Whitening of Bone Black in Oil Paint Films

part A

Characterization of the Deterioration of Bone Black in the 17th C Oranjezaal Paintings using Electron-Microscopic and Micro-Spectroscopic Imaging Techniques

ABSTRACT - A whitish deterioration product was observed on the dark paint in a number of large-scale oil paintings that are part of the Oranjezaal interior decoration in the Royal Palace of Huis ten Bosch (The Hague). The whitened areas of a painting by Pieter Soutman dating from 1648 were micro-sampled and compared with “healthy” black paint using different analytical imaging techniques. The dark paint was identified as bone black in linseed oil with a lead drier added. Microscopic images of the cross-section revealed a white top layer of 10-20 µm in the black paint layer. Imaging the cross-section surface with scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX) and specular reflection Fourier transform infrared (SR-FTIR) imaging showed homogeneous distributions of phosphate, phosphorus and calcium over the black and the white degraded bone black. X-ray diffraction (XRD) showed the presence of calcium phosphate hydrate (Ca₃(PO₄)₂·nH₂O), monetite (CaHPO₄) with possibly some poorly crystalline or amorphous hydroxyapatite (Ca₅(OH)(PO₄)₃). The EDX maps of lead and carbon, however, showed some discontinuity between the degraded and non-degraded bone black. There was an increase in the lead concentration in the white top layer, and a slight decrease of carbon. Transmission FTIR demonstrated that aromatic network polymers from the carbon black are markedly diminished in the white deterioration product. It is proposed that the carbonized organic matter in the bone black is vulnerable to photo bleaching in the presence of a lead catalyst under these circumstances.

keywords
Bone black; Carbon black; 17th-century oil paint; Pigment deterioration; Analytical imaging

1 This paper was presented at the 17th International Congress on X-Ray Optics and Microanalysis (ICXOM XVII), held in Chamonix, Mont Blanc, France, 22-26 September 2003, and is published in the special issue of Spectrochimica Acta Part B 59 (2004) 1601-1609, dedicated to this conference.
INTRODUCTION

The Oranjezaal is the central hall in the Royal Palace of Huis ten Bosch in The Hague (1647). The hall is decorated with large-scale paintings glorifying stadholder Frederik Hendrik, which were made in the period from 1648 to 1652 by various important seventeenth-century artists from the Northern and Southern Netherlands [Slothouwer 1945; Peter-Raupp 1980; Loonstra 1985]. The paintings consist of canvas paintings and painted vaults. The last conservation campaign (1998-2001) offered the opportunity to examine the paintings closely. A whitish deterioration product was observed on the dark paint in a number of oil paintings that are part of the Oranjezaal interior decoration scheme. Originally intended black and dark-brown areas, e.g., hair, eye pupils and shadows, have undergone dramatic changes in appearance. The alteration product appears as crust on top of the paint surface. Areas where the crust is thin have a bluish appearance due to the so-called ‘turbid medium effect’, i.e., a light tone will appear cooler when laid over a darker tone. Thicker areas look more yellowish. So far, a similar phenomenon has only been reported in fresco paintings [Marzetti and Scirpa 2000].

In this paper, we focus on a representative example that will be discussed in detail: the canvas painting Triumphal Procession with Gold and Silver by the Haarlem artist Pieter Soutman dating from 1648 [dimensions 3.85 x 2.10 m]. The whitened areas are marked in a detail of the painting showing the face and the hair of the man standing at the right (see Fig. 3.A.1). Not only the white spot in the hair is very striking, but also the eyebrow, the nose and mouth show whitish areas in the dark colors that were originally not intended. Several analytical techniques were used to characterize both the deteriorated and the unaffected original-black paint.

ANALYTICAL APPROACH

A minuscule paint sample (with a diameter of a few hundred micrometers) with the complete layer structure was taken from the whitened spot in the hair and then prepared as cross-section. This cross-section (A) was studied with different analytical imaging techniques and compared with a cross-section taken from a “healthy” black paint area in the same hair (B), the sample spots are indicated in Fig. 3.A.1. The nature of a paint system, i.e. its heterogeneity (we are dealing with multi-layer systems and with complex mixtures of inorganic and organic material), the minimum layer thickness and pigment particle size, requires a high spatial resolution (HR) of the instrumental techniques. The HR imaging techniques used here include visible and UV-fluorescence microscopy (LM), scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX) and specular reflection Fourier transform infrared (SR-FTIR) imaging. The advantage of this approach is that one can use the same paint cross-section for multiple investigation with all these imaging techniques. The techniques are complementary in the way that

---

2 The restoration was initiated by the State Building Department (Rijksgebouwendienst (Rgd), The Hague) and carried out by a large team of conservators under the supervision of the Limburg Conservation Institute (SRAL, Maastricht). Research on the painting technique and on specific paint defects started in the MOLART Program (1998-2002) and is being continued in the De Mayerne Program (2002-2004), both supported by the Netherlands Organization for Scientific Research (NWO, The Hague).
each technique reveals different additional information on the paint composition. The simplest imaging technique is light microscopy (LM). Its spatial resolution is limited to about 1 µm. It helps to reveal the layer build-up, morphology and pigment particle characteristics like shape, color and size. The spatial resolution of the electron microscope is even better than 1 µm. A backscattered electron image (BSE) of the cross-section shows the compositional contrast between and within the layers according to the atomic weight. A heavy element like lead is higher scattering (looks lighter gray) than a lighter element, like for example carbon or phosphorus or even calcium (looks darker gray). Apart from highly informative backscatter images, the EDX element maps show the distribution of the individual elements. Imaging FTIR gives information on the spatial distribution of characteristic chemical functional groups (like e.g. -CH, -OH, -C=O, CO₃, PO₄) in the paint cross-section. An area of 400 x 400 µm can be recorded simultaneously, which usually covers the whole cross-sectional surface. The spatial resolution is limited to 6-7 µm. Analytical results of imaging FTIR can be displayed as infrared spectra and false color or gray-scale images. Each spot or pixel contains an infrared spectrum. A false color plot shows the intensity distribution of a selected absorption band (in wavenumber) on the surface.

Besides the analysis of the cross-section, additional white material was very carefully scraped off from the paint surface and selected for transmission Fourier transform infrared (FTIR) and X-ray powder diffraction (XRD). Transmission FTIR
The whitening of bone black in oil paint films is more useful for the identification of organic material than specular reflection FTIR because of its low reflective properties. XRD helps to determine the crystal structure of the mineral phases, which comprises calcium phosphate compounds in the case described. The binding medium was analyzed with direct temperature resolved mass spectrometry (DTMS). DTMS is a fast fingerprinting mass-spectrometric technique and particularly suited for the recognition of classes of organic compounds in very small samples (microgram-scale): oil paint, resins, waxes, proteins and carbohydrates [Van der Doelen 1999; K.J. van den Berg 2000; J.D.J. van den Berg 2002].

EXPERIMENTAL AND INSTRUMENTAL

SAMPLE PREPARATION
Samples from the whitened area and from a “healthy” boneblack area were embedded in Technovit 2000 LC mounting resin, which is a one-component methacrylate that polymerizes under visible blue light (Heraeus Kulzer, Germany). After first grinding with silicone carbide (SiC) paper, the surface was dry polished with Micro-Mesh Sheets (Regular type, grades 1500 to 12,000; Micro-Surface finishing products inc., Wilton, Iowa, USA). Also, loose sample material was available to separate layers by micro-manipulating for DTMS analysis, single-point FTIR and XRD analysis.

MICROSCOPY
Microscopic studies on the paint cross-sections were performed on a Leica DMRX analytical microscope (Leica, Wetzlar, Germany). A 100W Halogen projection lamp provided normal reflected light in bright field and in dark field illumination. An Osram HBO 50 high-pressure mercury lamp and Leica filter D (excitation 360-425, emission > 460nm) were used for UV-fluorescence microscopy.

SEM-EDX
Scanning electron microscopy studies in combination with energy dispersive X-ray analysis (SEM-EDX) were performed on a XL30 SFEG high vacuum electron microscope (FEI, Eindhoven, The Netherlands) with EDX system (spot analysis and elemental mapping facilities) from EDAX (Tilburg, The Netherlands). Backscattered electron images of the cross-sections were taken at 20 kV acceleration voltage at a 5 mm-eucentric working distance and a spotsize of 3 that corresponds to a beam diameter of 2.2 nanometer with current density of approximately 130 pA. EDX analysis was performed at a spotsize setting of 4 (beam diameter 2.5 nm and current density 550 pA) to obtain a higher count rate. EDX Mapping parameters were: 512 x 400 matrix, 1028 frames, 70 µs dwell time and 35 µs amplitude time. Samples were carbon coated to improve surface conductivity in a CC7650 Polaron Carbon Coater with carbon fibre (Quorum Technologies, East Sussex, UK)
FTIR

Transmission spot analysis FTIR

FTIR analysis was performed on a Bio-Rad FTS-6000 FTIR spectrometer extended with a Bio-Rad UMA-500 IR Microscope (nowadays Digilab, Cambridge, MA, USA) and a single-point Mercury Cadmium Tellurium detector (4000-650 cm\(^{-1}\) range). Selected sample was applied onto a Graseby Specac P/N 2550 diamond cell (Graceby Specac, Orpington, Kent, UK) and analyzed in transmission mode. An empty diamond cell was used as a background. All single point spectra were recorded at 4 cm\(^{-1}\) spectral resolution, an undersampling ratio (UDR) of 2 and a mirror speed of 5 kHz. A total of 100 spectra were accumulated to increase signal to noise ratio (S/N). Data were processed using Win-IR Pro 2.5 software of Bio-Rad.

Specular reflection imaging FTIR

For the FTIR imaging the FTS Stingray 6000 system was used. It combines the above-mentioned spectrometer and microscope and a MCT detector (4000-1000 cm\(^{-1}\) range), which is a 64 x 64 pixels MCT Focal Plan Array system (Santa Barbara Focal Plane, California, USA). Images of the cross-section in a 400 x 400 \(\mu\)m area were recorded simultaneously at every mirror position of the step-scan interferometer at a spatial resolution of 6-7 \(\mu\)m. Imaging spectra were recorded at 16 cm\(^{-1}\) spectral resolution, an undersampling ratio (UDR) of 4 and a mirror step rate of 1 Hz. The step distance of the interferometer at UDR 4 was 1.266 \(\mu\)m. Approximately 500 interferosteps were needed to obtain the spectral resolution of 16 cm\(^{-1}\). The low step rate (1 Hz) allows the frame grabber board in the camera to average 200 images during each step, leading to a high S/N. A zink selenide (ZnSe) window was used for calibration and background. The resulting data-set contained 4096 interferograms, one for every pixel in the FPA. Further data processing was done using Bio-Rad Win-IR Pro software. The Kramers-Kronig transformation was applied to transform the specular reflectance spectra to absorbance-like spectra. Analytical results of the imaging FTIR system are displayed as infrared spectra and false color images or gray-scale images. Every spot or pixel in the cross-section image contains an infrared spectrum. A false color (or gray-scale) plot shows the intensity distribution of a specific absorption band on the surface of the cross-section.

DTMS

DTMS analyses were performed on a JEOL SXSU02A 4-sector double-focusing mass spectrometer (JEOL-Europe, Schiphol-Rijk, The Netherlands). Samples selected with a stereo-microscope were made into a suspension in a mini-mortar using aliquots of ethanol. The suspension was transferred to the Pt/Rh filament of the insertion probe and dried in vacuum. The probe filament was temperature programmed at a rate of 0.5A/min to an end temperature of about 800 °C. Compounds were ionized at 16eV under electron ionization conditions in an ionization chamber kept at 180 °C, mass analyzed over the range \(m/z\) 20-1000, with 1-s cycle time. Data were processed using a JEOL MP-7000 data system.
RESULTS AND DISCUSSION

DEGRADED WHITE BONE BLACK LAYER (A)
A schematic layer build-up of the whitened area is presented in Fig. 3.A.2. The canvas was first prepared with a beige-colored ground layer (layer 1). This ground is made up of lead white, a basic lead carbonate (2PbCO$_3$·Pb(OH)$_2$), with some additions of brown umber particles, an earth pigment containing hydrated iron oxide and manganese dioxide, in an oil medium. This is the typical preparation of the canvas paintings in the Oranjezaal [Groen and Van Loon 1999]. The next layer is a light-brown, semi-transparent paint layer containing white, red earth and brown pigment (layer 2). This second layer has the function of underpaint for the dark hair. The actual dark brown/black paint layer (layer 3) is quite a thick layer with large lumps of bone black and very little red earth. The binding medium of the black layer was determined with DTMS to be linseed oil. In the desorption part of the total mass spectrum, which is the low-temperature region, the main characteristics for drying oil were observed: \textit{m/z} 256 and 284 for palmitic acid (C16) and stearic acid (C18) respectively (ratio about 4 to 3). In the pyrolysis part of the total mass spectrum, which is the higher temperature region, the characteristic pattern of the pyrolysis products of the oil paint network was present. So we are dealing with a bone black in a drying oil system that has become whitish. By looking carefully at this layer 3 in the microscopic image, it becomes clear that the white deterioration product has formed not only a thin layer on top of the dark paint (indicated by the dashed line in Fig. 3.A.2), but that “white” bone black is also visible in some zones within the dark layer. This last observation was best seen in the UV fluorescence image of the cross-section. So the conclusion that can be drawn from LM is that indeed a color difference exists in both visible and UV light Microscopy between the whitened deterioration product and the normal bone black particles. The deterioration is concentrated in the top, although the whole layer is affected to some

Fig. 3.A.2 Schematic layer build-up of the whitened sample (A). (1) ground layer (50 µm). (2) light-brown underpaint layer (10-30 µm). (3) bone black layer (80-140 µm), the dashed line indicates the white top layer (10-20 µm).

Fig. 3.A.3 SEM backscattered electron image of the degraded bone black layer (A-layer 3). The dashed line indicates the white top layer.
extent. The next question investigated was whether a difference in chemical composition between whitened and normal bone black within layer 3 could be demonstrated.

The SEM-EDX images are illustrated in Figs. 3.A.3 and 3.A.4. The backscatter image of the degraded bone black layer (layer 3), see Fig. 3.A.3, gives little contrast, meaning little difference in composition, between the top and the rest of the layer. EDX spot analysis detected the same elements (calcium (Ca), phosphorus (P), carbon (C), oxygen (O) and some lead (Pb) and magnesium (Mg)) in the white top and in the lower part of layer 3. Calcium and phosphorus are characteristic of bone (and ivory) black. Bone black is made of charred bones and it contains mainly calcium phosphates and carbon black in an aromatic network [Winter 1983]. The origin from bone also explains the presence of a small amount of magnesium, atomic mass ratio to calcium 1:18. Ivory black, on the other hand, is made from charred ivory (elephant tusks), which, unlike bone, has a relatively high magnesium content. The atomic mass ratio of magnesium to calcium in ivory is around 1:8, which is twice as high as in bone [Freund 2002]. On the basis of this ratio, the black pigment is concluded to be bone black and not ivory black. Lead is from lead driers that the artist must have added to the black paint to speed up the drying of the oil paint, since such black pigments are known anti-oxidants and
The whitening of bone black in oil paint films

The role of lead was confirmed by DTMS. The EDX elemental maps in Fig. 3.A.4 visualize the distribution of elements over the black layer. There is an even distribution of Ca and P over the whole layer. However, the C and Pb maps show some differences between the top and the rest of the layer. The amount of carbon is slightly decreased in the top layer, but the lead intensity is higher towards the surface, which corresponds to the white top layer (indicated with dashed lines in Fig. 3.A.4), and, moreover, lead is also higher around some of the cracks. This may account for the slightly higher scattering (lighter gray) of the top layer in the SEM backscatter image.

Fig. 3.A.5 displays the imaging FTIR results. The left image is a plot of the embedding material that has a characteristic absorption at 1727 cm\(^{-1}\) originating from the carbonyl group. It outlines the position of the cross-section in the image. The middle image is a plot of the strong absorption peak at 1025 cm\(^{-1}\) that can be attributed to the phosphate groups (PO\(_4^{3-}\)) in bone black. They are intensive in the whole layer 3, but no difference could be observed between the top and the rest of the layer. This distribution absorbs a considerable amount of oil due to their porous structure.\(^3\) The porosity arises from the formation and escape of gases during carbonization [Winter 1983: 53-55; Mark et al. 1990].
of phosphate corresponds to the even distributions of the Ca and P elements over the layer that was shown in the EDX maps. There were no indications in the imaging FTIR data for the presence of other characteristic absorption bands like carbonate or metal carboxylate groups in the black paint layer 3. Carbonate is mainly restricted to the ground layer, as is shown in the right image of the strong absorption at 1405 cm$^{-1}$ of the carbonate group (CO$_3^{2-}$). The high concentration in this layer can be explained by the presence of lead white in this layer. Lead white is absent in the whitened top layer.

An XRD spectrum was taken of the white material that was separated from the surface. It was found that the white product contains a complex mixture of mineral compounds that are listed in Table 3.A.1.4 The source for the two calcium phosphate compounds, i.e., calcium phosphate hydrate (Ca$_3$(PO$_4$)$_2$·nH$_2$O) and monetite (CaHPO$_4$), is the original hydroxyapatite (Ca$_5$(OH)(PO$_4$)$_3$) in bone. The fate of hydroxyapatite when charring the bone seems clear from the medical, archeological and forensic literature [Hiller et al. 2003; Shipman et al. 1984]. The mineral component of the bone samples remains a hydroxyapatite during heating experiments up to 900 °C. No new forms of mineral phase are detected, but existing hydroxyapatite becomes more crystalline with heat and gives a more sharply defined XRD pattern [Shipman et al. 1984]. At this point we cannot really explain the detected calcium phosphate hydrate compound instead of hydroxyapatite. A certain amount of small and amorphous hydroxyapatite crystals in the paint would result in peak broadening and complicates the interpretation of the XRD spectrum. The reference spectra of bone heated at different temperatures are very illustrative in this respect [Shipman et al. 1984: 319]. In the temperature range of 300-400 °C when the carbonization (blackening) process takes place [Bennett 1999], the XRD spectrum of hydroxyapatite contains broad diffraction peaks. Another explanation could be that (some) hydroxyapatite is converted into another calcium phosphate compound under more acidic and/or humid conditions. Both possibilities will be investigated further. At least if some rearrangement of the crystal structure took place, this cannot account for the color change.

Some calcium carbonate is present in the white deterioration product in the form of aragonite. This could be a reaction product of excess calcium with atmospheric CO$_2$, because under such conditions (low temperature) aragonite is formed and not the more stable calcite mineral. The last compound that was detected with XRD, calcium formate (C$_2$H$_2$CaO$_4$), is very probably a reaction product. But the question is whether

Table 3.A.1 List of the mineral compounds that were identified with X-ray diffraction in the white deteriorated layer

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$_3$(PO$_4$)$_2$·nH$_2$O</td>
<td>calcium phosphate hydrate</td>
</tr>
<tr>
<td>CaHPO$_4$</td>
<td>monetite</td>
</tr>
<tr>
<td>CaCO$_3^{2-}$</td>
<td>aragonite</td>
</tr>
<tr>
<td>C$_2$H$_2$CaO$_4$</td>
<td>calcium formate</td>
</tr>
</tbody>
</table>

4 The XRD analysis was carried out by Peter Hallebeek at the Netherlands Institute for Cultural Heritage (ICN, Amsterdam).
it is of any significance for the degradation of bone black. It is difficult with XRD to distinguish between calcium formate and calcium oxalate. They are both reaction products of calcium ions with organic material and, according to the literature, oxalates are often detected on artistic works together with other degradation products, even if the visual effect of these salts is nil [Cariati 2000]. So they are not specific for bone black degradation. The conclusion drawn from the EDX, the imaging FTIR and XRD data about the inorganic substrate is that there is no change in the calcium phosphate composition that can account for the color change.

**Comparison with a Healthy Bone Black Layer (B)**

The degraded bone black layer was compared with a sample of a “healthy” bone black paint layer nearby. A schematic layer build-up of the black paint of the hair that overlaps the flesh color of the face in the sampled area is drawn in Fig. 3.A.6. On top of a beige-colored ground (layer 1), described above, a brown underpaint layer is applied (layer 2) and then a flesh tone layer containing lead white with some orange and red earth pigment and a few black particles (layer 3). The flesh layer is covered with a thin dark layer (layer 4) with bone black and some red lake and red earth similar in tone and transparency to layer 2. Layer 5 is the black paint layer with bone black and a small addition of red earth. It shows up as a dark layer in UV. The black layer looks intact, does not show cracks within the layer and the individual particles are still well recognizable, see backscatter image in Fig. 3.A.7. So this is assumed to be “healthy” bone black paint. EDX analysis detected the same elements as in the deteriorated sample: Ca, P, O, C and some Pb and Mg. Comparing the EDX elemental distributions (see Fig. 3.A.8) with the deteriorated sample shows one main difference. In the case of the “healthy” bone black layer, the lead is homogeneously distributed over the layer whereas in the deteriorated sample, we observed a higher concentration of lead in the whitened upper part.

Another comparison between the white deterioration product and “healthy” bone black paint was made with transmission FTIR. Both spectra are plotted in Fig.

---

**Fig. 3.A.6** Schematic layer build-up of the “healthy” black area (B). (1) ground layer (0-25 µm). (2) brown underpaint layer (7-25 µm). (3) flesh tone (25 µm). (4) thin brown layer (5 µm). (5) bone black layer (15-20 µm).

**Fig. 3.A.7** SEM backscattered electron image of the healthy bone black layer (B-layer 5).
3.A.9. The phosphate peak is the dominant peak in both spectra. This peak is scaled equally, because no change in the calcium phosphates was detected with SEM-EDX and imaging FTIR between the black and the white layer. The part between wavenumber 1650 and 1450 cm$^{-1}$ is characteristic of the aromatic carbon network [Pastorova et al. 1994]. This network is responsible for the black color of bone black. The two spectra in Fig. 3.A.9 illustrate that there is a significant decrease of aromatic network compounds in the white deterioration product. This might account for the color change from black to white. It is our interpretation that this aromatic network undergoes photo-oxidation to form oxidized compounds that are colorless, but contribute to the UV fluorescence of the top layer. But what could have triggered this reaction? UV light alone is insufficient to start the oxidation process, besides the levels are very low in the Oranjezaal. The reaction is possibly aided by the presence of lead that could act as a catalyst. SEM-EDX showed an increase in the concentration of lead ions in the white top layer. A possible source of this lead may be the driers that are presumed to be added inadvertently in an overdose in some areas of the paintings. We propose that lead has also migrated to the top layer. We intend to test this hypothesis further in a model experiment investigating

---

5 Protein chars made at FOM Institute AMOLF show similar characteristics. Personal communication with Freek Braadbaart, 2003.

6 Not unlike the appearance of lead soaps on the surface in paintings with problems of efflorescence [J.D.J. van den Berg 2002: 195-233].
The whitening of bone black in oil paint films

We have demonstrated that the whitish encrustation is not a layer deposited on the paint surface, but rather a transformation within the layer of the bone black pigment. There is a gradient in the degree of degradation in the layer: the white bone black is present in larger amounts towards the surface indicating that (UV) light and oxygen play a role in the decay process. We did not observe a conversion in the calcium phosphate substrate that could account for the color change. Imaging studies (FTIR and SEM-EDX) have shown that the phosphate, phosphorus and calcium distributions do not show a discontinuity between the black and the white layer. Structural analysis by XRD showed the presence of calcium phosphate hydrate ($\text{Ca}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$), monetite ($\text{CaHPO}_4$) with possibly some poorly crystalline or amorphous hydroxyapatite. The change in color from black to white is most likely attributable to decomposition of the organic component. FTIR demonstrated that aromatic network polymers from the carbon black are significantly diminished in the white crust. These aromatic carbon compounds are responsible for the black color. The proposed photo-oxidation is possibly aided by lead acting as a catalyst, because an increase in the lead concentration in the white top layer was observed.

**Fig. 3.A.9** Transmission FTIR spectra of the white deterioration product (A) and of the healthy bone black layer (B). The phosphate band at 1025 cm$^{-1}$ is normalized.

the vulnerability of bone black oil paint spiked with lead ions to photo-bleaching of the carbonized organic matter of bone.

**CONCLUSIONS**

We have demonstrated that the whitish encrustation is not a layer deposited on the paint surface, but rather a transformation within the layer of the bone black pigment. There is a gradient in the degree of degradation in the layer: the white bone black is present in larger amounts towards the surface indicating that (UV) light and oxygen play a role in the decay process. We did not observe a conversion in the calcium phosphate substrate that could account for the color change. Imaging studies (FTIR and SEM-EDX) have shown that the phosphate, phosphorus and calcium distributions do not show a discontinuity between the black and the white layer. Structural analysis by XRD showed the presence of calcium phosphate hydrate ($\text{Ca}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$), monetite ($\text{CaHPO}_4$) with possibly some poorly crystalline or amorphous hydroxyapatite. The change in color from black to white is most likely attributable to decomposition of the organic component. FTIR demonstrated that aromatic network polymers from the carbon black are significantly diminished in the white crust. These aromatic carbon compounds are responsible for the black color. The proposed photo-oxidation is possibly aided by lead acting as a catalyst, because an increase in the lead concentration in the white top layer was observed.
Chapter 3

ACKNOWLEDGEMENTS

We are indebted to Peter Hallebeek of the Netherlands Institute for Cultural Heritage (ICN, Amsterdam) for the XRD analysis and to Jerre van der Horst of the FOM Institute AMOLF for his assistance with the DTMS analysis. Lidwien Speleers is thanked for providing the paint cross-section of the whitened area (A).

REFERENCES


Van den Berg, J.D.J., 2000, Analytical chemical studies on traditional linseed oil paints, PhD dissertation University of Amsterdam, Molart Series (6), AMOLF, Amsterdam.


Van der Doelen, G.A., 1999, Molecular studies of fresh and aged triterpenoid varnishes, PhD dissertation University of Amsterdam, Molart Series (1), AMOLF, Amsterdam.


Loonstra, M., 1985, Het huijs int bosch / The Royal Palace Huis ten Bosch in a historical view, Amsterdam/Zutphen.


Slothouwer, P.F., 1945, De Paleizen van Frederik Hendrik, Leiden.

part B

The Whitening of Oil Paint Films containing Bone Black

Abstract - Whitish spots were observed in the dark paint of seventeenth-century oil paintings from the Oranjezaal (Huis ten Bosch, The Hague). As a result, the areas originally intended as black and dark brown—hair, eye pupils, shadows—have dramatically changed in appearance. Through chemical analysis, this color change is attributed to the degradation of bone black: the organic part responsible for the black color is decomposed. Other examples were investigated including a painted ceiling from the Johan de Witt House and two paintings by Rembrandt. Here, the whitening was caused by lead soap crystals or by degraded lakes in glazing surface layers.

Keywords
Bone black, Discoloration, Whitening, Oil paint, Lead migration, Lead soaps, 17th-century Dutch art, Chemical analysis

Introduction

The Oranjezaal, the central hall of the Royal Palace Huis ten Bosch in The Hague, is decorated with 39 large-scale allegorical paintings representing episodes from the life of stadholder Frederik Hendrik. Painted between 1648 and 1652, these are the works of twelve well-known artists from the Northern and Southern Netherlands [Loonstra 1985]. The last restoration (1998-2001) offered the opportunity to examine the paintings closely.8 They are remarkably well-preserved; only 4 of the 30 paintings on canvas are lined and previous restoration treatments are recorded. Nevertheless, natural ageing processes inherent to the materials available to artists in the seventeenth century have changed the original appearance of the paintings. The whitening of some black paints could not easily be accounted for and required further examination.9 This study includes several paintings from the Oranjezaal ensemble and selected examples from elsewhere.

---

7 This paper was presented at the 14th Triennial Meeting of ICOM Committee for Conservation, held in The Hague, The Netherlands, 12-16 September 2005, and is published in the Preprints Vol I 511-518.
8 The restoration was initiated by the State Building Agency (Rijksgebouwendienst (Rgd), The Hague) and carried out by a team of 25 conservators under the supervision of the Limburg Conservation Institute (SRAL, Maastricht).
9 So far, a similar phenomenon of whitening has only been reported in fresco paintings [Marzetti and Scirpa 2000].
In the Oranjezaal ensemble, severe degradation of dark tones is visible in works by Pieter Soutman, Gerard van Honthorst, Gonzales Coques, Pieter de Grebber, Jacob van Campen and Jacob Jordaens. The painting titles are listed in Table 3.2.1.10 Fig. 3.B.1 shows the complete loss of modeling in the hair of the triton in Frederik Hendrik’s Steadfastness by Van Honthorst (1650-52). This is the result of the partial whitening of the black paint. The alteration product appears here as white crust on the paint surface (Fig. 3.B.2). Areas where the crust is thin have a bluish appearance due to the so-called ‘turbid medium effect’, namely a light tone appears cooler when laid over a darker tone. Thicker areas look yellowish. In some paintings, the presence of white chunks in the dark paint results in a more spotty appearance. The color reversal from black to white has strongly altered the appearance of these paintings and presents many problems of visual interpretation and restoration treatment. Moreover, many paintings exhibit traces of harsh cleaning from past attempts to remove the white crust.

Optically similar surface phenomena were found on a painted ceiling (1655) from the Johan de Witt House in The Hague (Fig. 3.B.3) and on two paintings by

10 English translations are taken from Loonstra (1985). During the last restoration, it became evident that the portrait of Willem II in Frederik Hendrik in Triumph by Jordaens (No. 32) was not the work of Jordaens himself, but was in fact painted by Van Honthorst.
Rembrandt: *Portrait of a Standing Man* (1639) from the Staatliche Museen Kassel and *Homer* (1663) from the Royal Picture Gallery Mauritshuis (Table 3.B.1). The black profiles in the painted panel imitations on the wooden ceiling in the Johan de Witt House look quite distorted by a white degradation product on top (Fig. 3.B.4). This reduces the artist’s illusion of depth considerably. Because this ceiling painting has been neither varnished nor overpainted, it provides a unique case study.\(^{11}\) Rembrandt’s *Portrait of a Standing Man* has been the subject of earlier studies [Van der Weerd et al. 2002], but it was re-examined. The shadow below *The Standing Man’s* right arm, originally a dark tone, now has a primarily pale appearance, which is odd for a shadow. Whitening has also occurred in other parts of the same painting. This painting has undergone several restoration treatments in the course of time, including a lining. The painting of *Homer* suffered fire damage in the past, after which it was reduced in size [Broos 1987]. The dark paint layer reveals whitening in many places, which could have been caused by the fire.\(^{12}\)

---

11 The Johan de Witt House is property of the State Building Agency (Rijksgebouwendienst (Rgd), The Hague). The conservation of the ceiling paintings was carried out by Edwin Verweij et al. in 2003. Publication foreseen.

12 Rembrandt’s *Homer* is currently being restored by Petria Noble.
### Table 3.B.1 White surface layers: Summary of results of analysis

<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>Gerard van Honthorst, Frederik Hendrik's steadfastness, The Hague, 1650-52 canvas</td>
<td>Hair of triton HTBS 17x6</td>
<td>2. bone black, earth pigment, dispersed lead 1. lead white, umber</td>
<td>calcium phosphate</td>
<td>FTIR SEM DTMS</td>
</tr>
<tr>
<td>Oranjezaal</td>
<td>Jacob van Campen, Frederik Hendrik in battle commanding the waters, The Hague, 1651 canvas</td>
<td>Background under bridge HTBS 18x10</td>
<td>2. bone black, umber, red earth, dispersed lead (1. lead white, umber)</td>
<td>calcium phosphate</td>
<td>FTIR SEM DTMS</td>
</tr>
<tr>
<td>Oranjezaal</td>
<td>Gonzales Coques, Frederik Hendrik receiving survivance for Willem II, The Hague, 1650 (?) canvas</td>
<td>Armour of Frederik Hendrik HTBS 19x24</td>
<td>6. bone black, earth pigment, dispersed lead 5. red lake, red earth, bone black, dispersed lead 4. red earth, bone black, gypsum, dispersed lead 3. carbon black, organic brown, umber, red earth, lead white, chalk, gypsum 2. organic brown, carbon black, gypsum, lead white, red earth 1. lead white, umber</td>
<td>calcium phosphate</td>
<td>FTIR SEM</td>
</tr>
<tr>
<td>Oranjezaal</td>
<td>Gerard van Honthorst, Allegory on the marriage of Louise Henriette and the Grand Monarch of Brandenburg, The Hague, 1649 canvas</td>
<td>Hair of putti HTBS 21x15</td>
<td>4. bone black, dispersed lead 3. red lake 2. red lake, bone black, lead white 1. lead white, umber</td>
<td>calcium phosphate</td>
<td>FTIR SEM</td>
</tr>
<tr>
<td>Oranjezaal</td>
<td>Pieter Soutman, Part of the triumphal procession with prize gold and silver, The Hague, 1648 canvas</td>
<td>Hair of standing man HTBS 27x20</td>
<td>3. bone black, fine red earth, dispersed lead 2. lead white, chalk, red and brown earth 1. lead white, umber</td>
<td>calcium phosphate</td>
<td>FTIR SEM DTMS XRD</td>
</tr>
<tr>
<td>Oranjezaal</td>
<td>Jacob van Campen, Part of the triumphal procession with gifts from East and West, The Hague, 1649 canvas</td>
<td>Background HTBS 2001x25</td>
<td>1. bone black, red earth, dispersed lead</td>
<td>calcium phosphate</td>
<td>FTIR SEM</td>
</tr>
<tr>
<td>Oranjezaal</td>
<td>Jacob Jordaens, Frederik Hendrik in triumph, The Hague, 1650 canvas</td>
<td>Hair of Willem II HTBS 32x45</td>
<td>3. bone black, fine red earth, dispersed lead 2. organic brown, carbon black, earth pigment, dispersed lead 1. lead white, umber</td>
<td>calcium phosphate</td>
<td>FTIR SEM</td>
</tr>
<tr>
<td>Oranjezaal</td>
<td>Pieter de Grebber, The ascension of Frederik Hendrik into heaven, The Hague, 1651 wooden ceiling</td>
<td>Hair of putti HTBA 22A2</td>
<td>2. bone black, earth pigment, dispersed lead 1. lead white, earth pigment</td>
<td>lead soap crystals</td>
<td>FTIR SEM</td>
</tr>
<tr>
<td>Johan de Witt</td>
<td>Unknown, ceiling painting with panel imitation, The Hague, 1652-55 wooden ceiling</td>
<td>Black profile JdWp1.12 D4-Y</td>
<td>3. black paint: bone black, umber, dispersed lead 2. gray paint: lead white, carbon black 3. chalk ground</td>
<td>lead soap crystals</td>
<td>FTIR SEM DTMS</td>
</tr>
<tr>
<td>Oranjezaal</td>
<td>Pieter de Grebber, Part of the triumphal procession with spoils of war, The Hague, 1648 canvas</td>
<td>Leather boots highlight HTBS 24x43</td>
<td>3. chalk (earth pigment, bone black, carbon black, lead tin yellow) 2. bone black, red earth, chalk, umber, lead white (1. lead white, umber)</td>
<td>calcium carbonate</td>
<td>FTIR SEM</td>
</tr>
<tr>
<td></td>
<td>Idem, HTBS 24x44</td>
<td>Idem</td>
<td>3. chalk, carbon black, red earth, lead white 2. bone black, umber, lead white, chalk, red earth 1. lead white, umber</td>
<td>calcium carbonate, calcium oxalate lead chloride</td>
<td>FTIR SEM</td>
</tr>
</tbody>
</table>
The whitening of bone black in oil paint films

To characterize the composition of the white crust and its origin, samples were taken from areas discolored white as well as from control black paints surrounding the degraded zones. Sample material was mounted and prepared as paint cross-section to study with different mapping techniques: light microscopy, scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX) and specular reflection imaging Fourier transform infrared (SR-FTIR). Using these non-destructive techniques has the advantage that one can use the same paint cross-section for multiple investigations. Furthermore, discolored material was carefully scraped off the paint surface and selected for transmission FTIR and X-ray powder diffraction (XRD). The binding medium was analyzed with direct temperature resolved mass spectrometry (DTMS).

**METHODS OF EXAMINATION**

The black pigment from the degraded areas in the Oranjezaal paintings was consistently identified as bone black, which is made from charred bones. The results of the analysis are summarized in Table 3.B.1. DTMS determined the binding medium of the black paints to be linseed oil. The white alteration product was visible in the paint cross-sections as either a thin continuous top layer or individual discolored particles. The

---

14 The XRD analysis was done by Peter Hallebeek at the Netherlands Institute for Cultural Heritage (ICN, Amsterdam).
15 See footnote 13.
16 See also Ferreira et al. (2005).
white particles strongly fluoresced in ultraviolet light (UV), whereas black bone black particles appeared dark in UV. The particles had rounded edges with sizes up to 40 µm in diameter. The paint layers looked quite disrupted in cross-section, showing many cracks; these are probably now filled with varnish, as these zones were fluorescent in UV. Calcium and phosphorus were detected by SEM-EDX as the main elements present in the black as well as in the white-degraded bone black. Normal bone black contains about 10-20 per cent carbon, whereas the rest is mainly calcium phosphate. Imaging the cross-sectional surface with specular reflection FTIR confirmed the presence of strong phosphate absorption bands around 1050 cm\(^{-1}\). The maps revealed homogeneous distributions of phosphate, phosphorus and calcium over the black and white-degraded bone black.\(^{17}\) The XRD spectrum of the whitened material was interpreted as a mixture of calcium phosphate hydrate (\(\text{Ca}_3(\text{PO}_4)_2\cdot n\text{H}_2\text{O}\)), monetite (\(\text{CaHPO}_4\)), and possibly poorly crystalline or amorphous hydroxyapatite (\(\text{Ca}_5(\text{OH})(\text{PO}_4)_3\)). A conversion of the calcium phosphate substrate that would have accounted for the color change was thus not observed. The EDX maps of lead, however, showed discontinuity between the degraded and non-degraded bone black. In all the samples from the Oranjezaal listed in Table 3.B.1, the concentration of lead was increased in the whitened bone black. The inhomogeneity of the lead distribution is illustrated in a SEM backscattered electron image of a sample from a whitened spot in the hair of the triton of Frederik Hendrik’s Steadfastness by Van Honthorst (Fig. 3.B.5). We saw higher scattering (lighter gray) in the upper part of the layer where the bone black is discolored. Both SEM-EDX and DTMS indicated that the artists had added a lead drier to the black paint to accelerate the drying of the oil paint. Severe crack formation combined with lead remineralization along the edges was observed in some cross-sections (Fig. 3.B.5). Transmission FTIR

\(^{17}\) The phosphate, phosphorus, calcium and lead maps of sample HTBS 27x20 (see Table 3.B.1) are published in Van Loon and Boon (2004).
The whitening of bone black in oil paint films

The samples of degraded zones in the black profile from the Johan de Witt House contained bone black, but, in contrast to the Oranjezaal samples, the bone black itself was not altered. The white products were found to be lead soap crystals. Specular reflection FTIR data showed a strong absorption band of around 1530 cm\(^{-1}\), characteristic of lead carboxylates. SEM-EDX detected lead and carbon; in the backscattered electron image, the crystal structures of the lead soaps are evident (Fig. 3.B.6). Part of the lead soaps has crystallized within the bone black layer; the greater part, however, has migrated to the top and formed a deposit on the paint surface. The backscatter image suggests two lead sources: the lead drier in the bone black paint and the lower layer that contains lead white.

The cross-section of the Rembrandt from Kassel was re-examined. FTIR imaging and SEM-EDX showed the presence of calcium carbonate in the whitened top layer. Bone black is present in the layer underneath. The degraded layer was re-interpreted as a degraded yellow lake. In the painting of *Homer*, the whitened top layer suggests a degraded lake pigment as well. The lower layer consists of bone black mixed with some smalt and yellow lake.

Although the whitened black paints in the examples examined here all contain bone black, the analysis has proven that the white product may have different origins. The composition and nature of the bone black and the source and migration of lead is what merits attention at this stage to explain the different degradation behaviors of the bone black films.

---

18 The loss in carbon is supported by observations made with Infrared Reflectography (IRR) on *Frederik Hendrik in Battle Commanding the Waters* by Van Campen (No. 18): the white spots in the dark background reflected the light, whereas normal bone black absorbs the infrared light and appears dark in IRR.
Chapter 3

CHARRING PROCESS

The preparation of bone black is described in historic recipes [Marzetti and Scirpa 2000; Van de Graaf 1958]. Sheep, cow or pig bones are boiled in water to separate the fat; they are then carbonized in a closed ceramic container placed in an open fire oven at around 300 °C for 3 h; the container is slowly cooled; the bones are ground, dry and with water, into a very fine powder; the powder is washed in water and filtered. A black-brownish opaque material is thus obtained. What are the chemical reactions that take place during charring? To answer this question, we consulted literature of biomaterial research, as well as publications from archeology and forensics.

Fresh bone is composed of organic collagenous materials (about 25 per cent), inorganic materials (about 50 per cent) and hydration water (about 25 per cent) [Schultz 1997]. When heated under carbonization conditions (in the absence of oxygen), bone changes color subsequently from white to yellowish, to brown, to black, to gray, to white [Mayne Correia 1997]. The change in color is attributed to the decomposition of the organic component (collagen). Carbon signals are detected by Electron Spin Resonance in charred ivory heated above 200 °C, reaching a maximum at ca. 550 °C, after which the signal declines in intensity [Robins 1984]. In contrast, the mineral part of bone, which is hydroxyapatite, a calcium phosphate compound, is very stable at high temperatures: up to 1000 °C, no new forms of mineral phases are found, however, it becomes more crystalline and gives a more sharply defined XRD pattern [Shipman et al. 1984; Hiller et al. 2003].

So, it may be concluded that only part of the collagen is carbonized under the conditions used in the old recipes. Different qualities of bone black existed depending on the heating conditions, especially temperature and time of exposure. From the nineteenth century, the production of bone black was industrialized, which resulted in a more uniform and stable pigment. We repeated the experiment in the laboratory by heating animal bones and pure collagen in an oven at 300 °C for three hours. A black product was obtained this way. The transmission FTIR spectra displayed aromatic features that increase while some starting material remained. The porosity and large surface area of bone black develop by the formation and escape of gases during carbonization. After carbonization the amount carbon is reduced to 10-20 per cent by mass and the mineral phase is 70-80 per cent by mass. The carbon is distributed throughout a porous structure of hydroxyapatite in the bone char.

LEAD MIGRATION

When mixing carbon blacks into paint, they take up an incredible amount of oil (almost 1:1) due to their porous structure and large surface area. This makes carbon black paints highly medium-rich. Since carbon blacks are known antioxidants that retard the drying of oil paint films, lead driers were added to the oil to speed up the drying process. Evidence of these kinds of addition is present in historical sources [Van de Graaf 1958]. These two properties of bone black films fulfill some of the conditions that promote
The whitening of bone black in oil paint films

The formation and migration of organolead compounds towards the surface. The ceiling painting in the Johan de Witt House is an extreme example of this phenomenon with lead carboxylates deposited on the surface. The SEM backscatter image illustrates well-developed crystal structures (Fig. 3.B.6). Since the ceiling was untouched for centuries, the metal carboxylate crystals had time to develop and accumulate on the surface. In the Oranjezaal samples, the relative amount of lead is increased (about 200 per cent) inside the whitened bone black particles. It is trapped in the porous and strong-adsorbing bone black particles, and not on the surface, because, unlike in the Johan de Witt ceiling, there is a varnish layer present acting as a barrier. The ability of bone char to adsorb metal ions is well known and is, for example, exploited for cleaning wastewater [Ko et al. 2004]. It is proposed that lead plays an important role in the degradation process of the aromatic carbon compounds in bone black, as a catalyst or a reactant. It is of interest in this respect to mention at least one historical source on the incompatibility of lead compounds with bone black [Marzetti and Scirpa 2000].

In a reconstructed paint composed of vine black, lead acetate drier, and linseed oil, lead was found to migrate towards the top of the paint layer. Lead acetate crystals caused air bubbles in the paint, which could explain the cracks. The severe crack formation combined with lead remineralization along the edges observed in cross-sections from Oranjezaal paintings looks very similar to cross-sections of the reconstructed black paint (Compare Figs. 3.B.5 and 3.B.7). We conclude that extra lead drier was added to the black paints in the Oranjezaal.

**Discussion**

The results so far demonstrate that the whitish “encrustation” in the paintings from the Oranjezaal is not a layer deposited on the paint surface, but rather a chemical transformation within the layer of the pigment bone black. This observation has direct consequences for the restoration treatment, as the white product is an original part of the painting. There is a gradient in the degree of degradation in the layer: the white bone black is present in larger amounts towards the surface, which indicates that (UV) light and oxygen, as well as moisture and temperature, play roles in the decomposition process. A conversion in the calcium phosphate substrate that could account for the color change was not observed. The change in color from black to white is presently attributed to decomposition of the organic component. FTIR demonstrates that aromatic network polymers from the carbon black are significantly diminished in the white crust. These aromatic carbon compounds are responsible for the black color. The decomposition of the organic component is possibly aided by lead in the bleached top layer that acts as a catalyst or reactant.

In a previous study, the calcium carbonate deposit on the bone black layer in the sample of the *Portrait of a Standing Man* was interpreted as a thermal degradation

---

19 The reconstructed paint (ZBAC) was made by Leslie Carlyle during a MOLART Fellowship in 1999.  
20 Information provided by Leslie Carlyle.
product of bone black. However, with more knowledge now on the composition of bone black, it is understood that the mineral phase is very stable at high temperatures and that it does not convert to calcium carbonate. So, it is more likely that the presence of calcium carbonate in the whitened top layer points to a degraded yellow lake glaze. The absorption band at 1620/30 cm\(^{-1}\) can then be interpreted as an aromatic feature, which is expected to derive from the organic dye. The same feature was encountered in specular reflection spectra of red lake pigments and of Kassel earth.\(^{21}\)

Specular reflection FTIR imaging turned out to be an effective technique to characterize the nature of the alteration product directly on the paint cross-section. It enables the distinction between strong absorption bands of phosphates, carbonates and carboxylates.

CONCLUSION

The dramatic change in color from black to white observed in the seventeenth-century oil paints is attributed to the presence of bone black used as pigment in the paint film. The whitening, although optically similar, turns out to have different causes. In the two paintings by Rembrandt, degraded glaze layers of yellow lake pigments applied on the black layer are considered responsible for the now rather blanched appearance of the bone black films. The efflorescence on the surface of the ceiling painting from the Johan de Witt House is the result of migration and crystallization of lead soaps. In the paintings from the Oranjezaal, calcium phosphate was found as the white product. It is proposed that the carbonized organic matter in bone black has reacted away under these circumstances. The increase in the concentration of lead in pale bone black points to an important role of lead in the reaction process. The conditions under which the bone black is made are very likely to have influenced the stability of the pigment. More research is currently being carried out on the nature of the organic components that form during charring to find out how they react.

ACKNOWLEDGEMENTS

We would like to thank the following for making sample material available: Hans Brammer, Staatliche Museen Kassel; Leslie Carlyle, Netherlands Institute for Cultural Heritage; Petria Noble, Royal Picture Gallery Mauritshuis; Lidwien Speleers, FOM Institute AMOLF; Edwin Verweij, VERWEIJ / Office for Architectural Paint Research & Conservation Amsterdam. We thank Jerre v/d Horst of the FOM Institute AMOLF for assistance with DTMS analysis and Peter Hallebeek of the Netherlands Institute for Cultural Heritage for XRD analysis.

---

\(^{21}\) Unpublished observations.
REFERENCES


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
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 H₂S 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.
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/floatation, 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 Tripenhuis, 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 Tripenhuis 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 Tripenhuis 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, (Tripenhuis, 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 harder (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.
White hazes and surface crusts on dark oil paints inc., Wilton, Iowa, USA). Extra care was taken in preparing cross-sections for specular reflection FTIR imaging, a highly surface-sensitive technique (see also Chapter 1).

**INSTRUMENTATION**

A Leica DMRX microscope was used for visual interpretation of the layer build-up of the cross-sections. Specular reflection FTIR imaging was done using the Biorad FTS Stingray 6000 system, with a 64x64 pixels MCT Focal Plane Array detector. Raman spectroscopy was carried out together with Silvia Centeno at the Scientific Department of the Metropolitan Museum New York. The Raman spectra were recorded with a Renishaw System 1000 spectrometer using lasers with $\lambda = 785$ nm and $\lambda = 514$ nm. Static SIMS experiments were performed on a Physical Electronics Trift-II time-of-flight SIMS. The embedded samples were carbon coated in a CC 7650 Polaron carbon coater prior to SEM-EDX analysis to improve the surface conductivity. SEM-EDX analysis was performed on a FEI XL30 SFEG high vacuum electron microscope coupled with EDAX detector. Isolated samples were also analyzed using single-point transmission FTIR and DTMS. Single-point transmission FTIR was performed on a Biorad FTS-6000 FTIR spectrometer extended with a Biorad UMA-500 IR Microscope. Selected sample material was applied onto a Graseby Specac P/N diamond cell. DTMS analysis was carried out using a JEOL JMS-SX/SX102A 4-sector double-focusing mass spectrometer. Selected sample was made into suspension with ethanol, and transferred to the filament of the insertion probe. See the experimental section in Chapter 1 for more technical and instrumental details.

**EXAMINATION OF THE WHITENING: PAINTING STUDIES**

A summary of the results of analysis is given in Table 4.2. 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 PROCESION 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
Fig. 4.1.1 Pieter de Grebber, *Part of the Triumphant 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). 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 ν(CO₃²⁻). 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

---

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 oxalates is the sharp peak 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

---

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 1061 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

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 cochinale and brazilwood) and 3A2 (in combination with Mexican cochinale 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. 4.1.3 FTIR imaging data of cross-section HTBS 24x44.

Fig. 4.1.4 SEM backscatter and EDX spectrum of a lead chloride product deposited at the paint surface.
calcium carbonate particles, possibly as substrates of a now faded brazilwood and/or other red lake pigment, in addition to fine red earth.\(^\text{10}\)

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.

**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 *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 *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\(_4^3\)) at c.1050 cm\(^{-1}\) overlays the dark layer. EDX detected the elements calcium and

---

\(^{10}\) 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 $c$.1519 cm$^{-1}$, characteristic of the asymmetric lead carboxylate group $\nu_a$(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 $\nu_a$(CH$_2$) and $\nu_s$(CH$_2$), manifest in the 2900 cm$^{-1}$ region.
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.
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. Speleers). 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
White hazes and surface crusts on dark oil paints

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 Gregger, 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
Chapter 4

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.
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.\footnote{Johan de Witt House is property of the State Building Agency (Rijksgebouwendienst (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.}

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.\footnote{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.} 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
high temperatures, some lead is detected at m/z 206-208, and phosphorus typical of bone black at m/z 62 (P$_2$) and 124 (P$_4$). Bone black can be distinguished from other carbon blacks by its high content of calcium phosphate matter. The FTIR image of the phosphate group (PO$_{4}^{3-}$) 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 ν$_a$(COO). 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.
White hazes and surface crusts on dark oil paints

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, pateuze 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 (doedverf), 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 \(\nu(\text{CO}_3^{2-})\). 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

---

\(^{14}\) Chalk in oil produces a translucent brown, different from chalk in animal glue. Personal communication, 2004, Leslie Carlyle and Maartje Witlox, HART Project De Mayerne Research Program 2002-2006.
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.\textsuperscript{15} 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.\textsuperscript{16}

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\(^{-1}\) \(\nu_2\) (COO) and a weak, sharp one at c.
1320 cm\(^{-1}\) \(\nu_s\) (COO) is very characteristic of calcium oxalates [Cariata 2000].\textsuperscript{17} 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.\textsuperscript{18} 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

\textsuperscript{15} Analyses carried out by the author (e.g. HTBS 6x4, 26A9, 27x23).


\textsuperscript{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.

\textsuperscript{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. 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]. Originally, the painting was much larger, including two scribes. 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. The lower

19 See footnote 5.
20 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 All that remains of only one of them are two fingers holding a pen at the lower right.
22 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.\textsuperscript{23} Samples from different areas in the painting were taken before treatment and prepared as paint cross-sections for LM, specular reflection FTIR imaging, Raman microscopy, and SEM-EDX studies.\textsuperscript{24} Additional analysis of a scraping of the white crust was carried out using single-point FTIR transmission spectroscopy.\textsuperscript{25} 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 orangey 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\textsuperscript{26}-, 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.\textsuperscript{27} 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,
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 \(\nu(SO_4^{2-})\) [Derrick et al. 1999]. In addition, the FTIR spectrum indicates some carbonate salts among the components present in the crust. The bands at \(c.1390 \text{ cm}^{-1} \ \nu(CO_3^{2-})\) and \(c.680 \text{ cm}^{-1} \ \nu(CO_3^{2-})\) are indicative of lead carbonate, whereas the band at \(c.1429 \text{ cm}^{-1}\) can be ascribed to calcium (and potassium?) carbonate. Furthermore, the band present at \(c.1560 \text{ cm}^{-1}\) can be assigned to the asymmetric stretch vibration of potassium soaps \(\nu_a(COO)\). Calcium oxalates also contribute to the FTIR spectrum of the white crust with absorption bands at \(c.1637 \text{ cm}^{-1} \ \nu_a(COO), c.1320 \text{ cm}^{-1} \ \nu_s(COO)\), and \(c.780 \text{ cm}^{-1} \ \nu(OCO)\).\(^{28}\) Usually the most characteristic absorption for calcium oxalates is the sharp peak at \(c. 1320 \text{ cm}^{-1}\). 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

\(^{28}\) 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 1009 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 Kees 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 584s18), 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 ($K_2SO_4$), 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

---

30 Potassium was added in ancient glass to decrease the melting point.

31 According to Muhlethaler and Thissen, the principle cobalt ores used in the manufacture of smalt in the 17th century were smaltite ([Co,Ni]As$_3$)$_n$, erythrite ([Co,Ni],[AsO$_4$]$_2$).H$_2$O) and cobaltite (Co,Fe)AsS [Muehlethaler and Thissen 1993: 113-115]. See also Riederer [Riederer 1968].
White hazes and surface crusts on dark oil paints

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.

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].
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.
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/
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), 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.

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 (Kp) at 25 °C are, for example, 2.32x10⁻⁹ for CaC₂O₄·H₂O, 8.7x10⁻⁹ for CaCO₃, 1.6x10⁻⁸ for PbSO₄, and 5x10⁻¹⁴ and PbCO₃.
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.
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 particels in the priming layer (*right*).
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’ (1655-65) BY PHILIPS WOUWERMAN FROM THE ROYAL PICTURE GALLERY MAURITSHUIS

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 orangey 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 ‘schietyellows’ 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.42 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.43 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.44 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,

---

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.
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).
White hazes and surface crusts on dark oil paints

‘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).
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).
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 investigation\(^{49}\), 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 Jongsma | Bureau voor Kleuronderzoek en Restauratie Amsterdam.
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

---

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>
<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>
</table>
| Oranjezaal, The Hague | Pieter de Grebber  *Part of the Triumphal Procession with Spoils of War (No. 24)*, 1648 canvas | Leather boots highlight HTBS 24x43 | 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) | calcium carbonate | LM FTIRima SEM |
| Oranjezaal, The Hague | Pieter de Grebber  *The Ascension of Frederik Hendrik into Heaven (No. 22)*, 1649 wooden ceiling | Hair of putti HTB 22A2 | 2. dark brown paint: bone black, earth pigment, dispersed lead  
1. light-brown paint: lead white  
(saponified), earth pigment | lead soaps lead sulfate | LM FTIRima SEM |
| Oranjezaal, The Hague | Salomon de Bray  *Part of the Triumphal Procession with Musicians (No. 26)*, 1649 canvas | Dark brown jacket of old man HTBS 26x1 | 5. translucent grayish layer: chalk, carbon black  
3, 4. dark brown paint: carbon black, red earth, chalk, dispersed lead  
2. reddish paint: red earth, carbon black, organic brown, lead white, chalk, umber  
1. beige-colored ground: lead white, umber | calcium carbonate calcium oxalate lead chloride | LM SEM |
| Johan de Witt, The Hague | Unknown Artist  ceiling painting with panel imitation 1652-55 wooden ceiling | Black profile JDWP1.12 D4-Y a, b, c | 3. black paint: bone black, umber, dispersed lead  
2. gray paint: lead white, carbon black  
1. chalk ground | lead soaps (lead sulfate) | LM FTIRima Raman SEM FTIRdm DTMS |
| Staatliche Museen Kassel | Rembrandt van Rijn  *Portrait of a Standing Man (GK 239)*, 1639 canvas (lined) | Background GK 293x3 | 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 | calcium carbonate calcium oxalate lead chloride | LM FTIRima Raman SEM |
| Mauritshuis, The Hague | Rembrandt van Rijn  *Homer (MH 584)*, 1663 canvas (lined) | Dark garment lower edge, centre black brushstroke MH 584x04, s19 | 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) | Lead-potassium-sulfate calcium oxalate | LM FTIRima Raman SEM FTIRdm DTMS |
<p>| | | | | idem |LM FTIRima Raman SEM |</p>
<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>Cap</td>
<td>Rembrandt van Rijn, Homer (MH 584)</td>
<td>MH 584x06</td>
<td>3. translucent orange paint: smalt, red earth, dispersed lead (bone black)</td>
<td>idem</td>
<td>LM SEM</td>
</tr>
<tr>
<td></td>
<td>1663 canvas (lined)</td>
<td></td>
<td>2. dark brown undermodelling: smalt, bone black, red earth, dispersed lead</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1. second ground: lead white (saponified), chalk, earth pigment, black</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dark garment</td>
<td></td>
<td>MH 584x09</td>
<td>5. dark brown paint: smalt, bone black, red earth, dispersed lead</td>
<td>idem</td>
<td>LM SEM</td>
</tr>
<tr>
<td>lower left</td>
<td></td>
<td></td>
<td>4. intermediate varnish</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3. reddish brown undermodelling: umber, red earth, bone black, lead white/dispersed lead, yellow lake</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2. second ground: lead white (saponified), chalk, earth pigment, black</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1. first ground: chalk, earth pigment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dark garment</td>
<td></td>
<td>MH 584x23</td>
<td>5. paint</td>
<td>idem</td>
<td>LM SEM</td>
</tr>
<tr>
<td>fire-damaged</td>
<td></td>
<td></td>
<td>4. undermodelling</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3. intermediate varnish</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2. black sketch</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1. second ground: lead white (saponified), chalk, earth pigment, black</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Left hand</td>
<td></td>
<td>MH 584x35</td>
<td>4. thin layer: smalt-rich</td>
<td>idem</td>
<td>LM SEM</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3. reddish paint: red earth, bone black, red lake, organic brown (Kassel earth?)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2. dark brown undermodelling: bone black, earth pigment, dispersed lead, lake?</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1. second ground: lead white (saponified), chalk, earth pigment, black</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Left sleeve</td>
<td></td>
<td>MH 584x51,</td>
<td>3. translucent orange-brown paint: red lake, organic brown (Kassel earth?), red</td>
<td>idem</td>
<td>LM SEM</td>
</tr>
<tr>
<td>fire-damaged</td>
<td></td>
<td>s30</td>
<td>earth, smalt, bone black, dispersed lead</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2. intermediate varnish</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1. second ground: lead white (saponified), chalk, earth pigment, black</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Left sleeve</td>
<td></td>
<td>MH 584x56</td>
<td>2. paint: smalt, bone black, red earth, lakes?, organic brown (Kassel earth?)</td>
<td>idem</td>
<td>LM Raman</td>
</tr>
<tr>
<td>Fire-damaged</td>
<td></td>
<td></td>
<td>dispersed lead</td>
<td></td>
<td>SEM</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1. second ground: lead white (saponified), chalk, earth pigment, black</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dark garment</td>
<td></td>
<td>MH 584x65</td>
<td>6. black paint: bone black, smalt, yellow lake, red earth, dispersed lead</td>
<td>idem</td>
<td>LM SEM</td>
</tr>
<tr>
<td>lower left</td>
<td></td>
<td></td>
<td>5. intermediate varnish</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4. reddish undermodelling: red lake, carbon black/organic brown?, red earth, dispersed lead, bone black</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3. black sketch: bone black, red earth, lake?, (smalt)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2. second ground: lead white (saponified), chalk, earth pigment, black</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1. first ground: chalk, earth pigment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Collection</td>
<td>Artist, title, date and support</td>
<td>Sample no.</td>
<td>Paint composition</td>
<td>White product</td>
<td>Analysis</td>
</tr>
<tr>
<td>------------</td>
<td>---------------------------------</td>
<td>------------</td>
<td>-------------------</td>
<td>---------------</td>
<td>----------</td>
</tr>
<tr>
<td>Mauritshuis The Hague</td>
<td>Rembrandt van Rijn <em>Simeon's Song of Praise (MH 145)</em> 1631 oak panel</td>
<td>Gray floor MH 145x01A</td>
<td>3., 4. 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>Philips Wouwerman Departure from the stable (MH 215) 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></td>
<td>Frans Hals Portrait of Jacob Olycan (MH 459) (1596-1638) 1625 canvas (lined)</td>
<td>Black drapery and gray background MH 459x4a, s01, s02, s05, s06</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 FTIR dm DTMS</td>
</tr>
<tr>
<td>Tripenhuis 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>
White hazes and surface crusts on dark oil paints

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 Tripopenhuis 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 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 ‘schiet-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

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

a redwood) [Saunders and Kirby 1994]. 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 goun 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 Oranjelaal 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 brazilein. 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\(^{-1}\) \(\nu(CO_3^{2-})\), the FTIR spectra show prominent bands at c.1640 cm\(^{-1}\) \(\nu(COO)\) and c.1326 cm\(^{-1}\) \(\nu(COO)\) 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 1643, 1330 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.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.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

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 Katrien Keune, scientist, 2006.

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 Triumphant 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 (Pb₄Cl₁₄(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 Pb : Cl of 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

---

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 *Simeon’s 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.
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 watersoluble 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 off 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.

1. Formation of metal soaps
2. Migration towards surface by RH / T
3. Interaction at surface with CO₂, SO₂, etc.
4. Mineralization and crust grows thicker

metal soap
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

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 °C) [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 °C), 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 hardness 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 carboxyalates 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.

---

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

[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].

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 possible 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\(^{69}\)) 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-siccated 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

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^{-8} 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).\textsuperscript{73} 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 [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.

\textbf{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 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 Homer is also associated with the extensive/excessive use of smalt in the dark translucent paint.

\textsuperscript{73} 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 [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 [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 [Groen 1997; Noble and Van Loon 2005; see also Chapter 2].
layers. 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 Grebber’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 Grebber 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

---

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
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.

ACKNOWLEDGEMENTS

We wish to thank the following for making sample material available and for useful discussions: Hans Brammer, Staatliche Museen Kassel; Petria Noble, Royal Cabinet The Mauritshuis; Lidwien Speleers, FOM Institute AMOLF; Alice Tate-Harte, Royal Cabinet The Mauritshuis; Johanneke Verhave, Royal Cabinet The Mauritshuis; Edwin Verweij, Office for Architectural Paint Research and Conservation Amsterdam. We are grateful to Silvia Centeno, Metropolitan Museum New York, for her kind help with Raman microscopy. We thank Jerre van de Horst, FOM Institute AMOLF, for his assistance with the DTMS analysis. We are also indebted to Jo Kirby, National Gallery
REFERENCES

Van den Berg, J.D.J., 2002a, ‘Studies on the composition and formation of bloom on primed canvas used by F.E. Church and on paint in works of art by F. Stella’, in Analytical chemical studies on traditional linseed oil paints, PhD dissertation University of Amsterdam, Molart Series (6), AMOLF, Amsterdam, pp. 195-233.
White hazes and surface crusts on dark oil paints


Keune, K., 2005a, ‘Metal soap aggregates in oil paintings from the 15th-20th century’, in Binding medium, pigments and metal soaps characterized and localized in paint cross-sections, PhD dissertation University of Amsterdam, Molart Series (11), AMOLF, Amsterdam, pp. 128-132.

Keune, K., 2005b, ‘Secondary ion mass spectrometry characterisation of traditional oil paint: comparative studies with DTMS and GC/MS’, in Binding medium, pigments and metal soaps characterized and localized in paint cross-sections, PhD dissertation University of Amsterdam, Molart Series (11), AMOLF, Amsterdam, pp. 44-66.


White hazes and surface crusts on dark oil paints


Chapter 4


White hazes and surface crusts on dark oil paints


Darkening as a result of Increased Transparency in 17th C Oil Paintings

ABSTRACT – This chapter focuses on increased transparency and consequent darkening of seventeenth-century oil paint films, as yet another aspect of metal soap formation that degrades the appearance of paintings. Several paintings are presented from the collection of the Royal Picture Gallery Mauritshuis The Hague and painted ceilings from the Trippenhuis Amsterdam. Reduced scattering/hiding power, as a result of the transformation of particulate lead white or lead-tin yellow pigment into amorphous lead soaps, explains the increased transparency and darkening observed on the paint surfaces. This can occur in underlying and surface oil paint layers, but can also occur selectively in specific areas associated with the wood grain resulting in disturbing stripy patterns of dark lines. The phenomenon can affect pictures to different degrees, also depending on the color of the affected layer and the presence of a dark underlayer. A color change due to loss of the lead white component is most noticeable in medium brown and gray tones and, when mixed with smalt, in blue paints. As with the localized darkening on the wood grain, the thickness and absorbency of the chalk ground, degree of swelling and transparency of the painting technique also appear to be decisive factors in the final appearance of the pictures.

INTRODUCTION

Already towards the end of the seventeenth century, the Dutch painter Gerard de Lairesse observed the phenomenon of increased transparency with regard to oil paint layers. He explicitly mentioned it in his Groot Schilderboeck published in 1707 [Van Eikema Hommes 1998]. In the nineteenth-century literature, authors often remarked that oil paint will become transparent and grow darker, and that “dark grounds will devour the colors in time” [Carlyle 2001: 177-78, 261]. There are countless pictures, where increased transparency of lead-white containing paint films allow underdrawing, underpainting or artist alterations to become more visible than originally intended (most pentimenti involve the use of lead white). Although in some cases underlying layers were meant to be visible, in paintings such as Adriaen Coorte’s Still Life with Asparagus (Rijksmuseum, Amsterdam inv. no. A-2099) from 1697, there is no doubt that the underlying dark background that has become disturbingly visible through the asparagus’ tips is due to the lead-white- containing paint of the asparagus having become more translucent.1

In much of the conservation literature, increased transparency of oil paint has been ascribed to a rise in the refractive index (RI) of the oil binding medium with age (1.48

---

1 In addition to increased transparency, tiny craters filled with a whitish substance (corresponding to the phenomenon of metal soap aggregates) were observed [Van Eikema Hommes 1998: 118 and 2004a: 38; Wallert 1999: 94].
for fresh linseed oil compared to 1.57 for a very mature paint film). This was largely based on experiments in the 1920s and 30s by the British chemist A.P. Laurie [Laurie 1926]. However, for pigments with a high RI, such as lead white (RI: 1.9-2.1), this rise is not enough to explain the increased transparency observed in many paint films. Already in 1909, the German chemist Alexander Eibner, who was active with painting studies in Munich, suggested that increased transparency of lead white paints was a result of the formation of lead soaps [Eibner 1909: 121]. Gettens and Stout cite the work of Eibner in this regard [Gettens and Stout 1966: 175]. In 1967, Laurie admitted that the increase in transparency may in part be due to chemical change, also noting that when there is darker paint below, the picture will decrease in tone [Laurie 1967: 110, 140-155]. Rees Jones in 1991 calculated the effect of the age-induced increase in the transparency of oil paint, correctly observing that thinly painted pictures with a dark ground or underlayer are worst affected [Rees Jones 1991]. Townsend in 1993, pointed out that the change in refractive index is too small to account for the change in appearance and that it must be the RI of the pigment that alters, possibly as a result of a chemical change occurring on the surface of the particles from an interaction between the oil and the lead pigment [Townsend 1993].

Metal soap-related oil paint degradation has been the subject of recent painting studies (1998-2007), where the dissolution of lead white in association with lead soap aggregates was noted in cross-sections of the affected ground layers of Rembrandt’s Anatomy Lesson of Dr. Nicolaes Tulp from 1632 (The Hague, Mauritshuis inv. no. 146) [Boon et al. 2002; Keune 2005a]. More recently, it was found that the conversion of lead white to amorphous metal soap complexes also plays a major role in the increased transparency of oil paint films [Noble, Van Loon and Boon 2005 and 2007]. Due to saponification of lead white the light scattering properties of the paint are reduced and light can penetrate deeper into the paint layer, creating a localized darkening effect particularly when a non-reflecting paint or ground (or panel) is present below. In medium to dark paint mixtures, color change is also noticeable due to loss of the white component in the paint mixture. These results were also supported in a recent study on metal soap-related color and transparency changes in two nineteenth-century paintings where localized darkening was ascribed to the formation of lead and zinc soaps. Here, the degree of darkening was found to be not only dependent on the degree of saponification, but also on the color of the affected layer and the presence of a dark underlayer [Shimadzu and Van den Berg 2006]. Furthermore, darkening can occur selectively in specific areas where it is associated with the ground that fills the uneven structure of the support. Various causes and names have been touted to describe this phenomenon, including linear staining, ground staining and variable translucency [Zucker and Boon 2007]. In panel paintings, it is often generally seen as abrasion or possibly even as part of the artist’s technique. However, after microscopic examination it becomes clear that the darkened lines, that are clearly associated with the wood grain, are not due to exposure of the wood itself, but rather to alteration of the ground layers that had become transparent and darkened. Not only do these darkened grounds have a strong visual impact when they shimmer through the overlying layers, but they can
become even more exposed as a result of volume changes in the affected layer that causes the overlying surface paint in these areas to flake off.

In this chapter, case studies examined (2002-2007) with regard to metal soap-related transparency changes in seventeenth-century oil paintings are presented. The paintings are listed below (Table 5.1). The metal-soap related degradation includes A: increased transparency of lead-tin yellow paints, B: darkening of medium brown and gray tones, C: selective darkening of ground layers associated with the wood grain and D: darkening/browning of blue paints containing lead white and smalt. Cross-sections were studied with analytical microscopic techniques, including scanning electron microscopy coupled with energy dispersive X-ray elemental analyses (SEM-EDX) and specular reflection Fourier transform infrared imaging (FTIR imaging), to demonstrate the conversion to lead soaps in the paint layers. Isolated samples of the ground and paint were also analyzed with direct temperature resolved mass spectrometry (DTMS) to characterize the binding media. In this chapter, the lower ground is referred to as the chalk ground and the dull-colored oil bound second ground, the *imprimatura*. This build up of preparatory layers, consisting of a single oil-bound *imprimatura* of lead white colored with small amounts of other pigments, applied on top of a lower chalk/glue ground, is typical for Dutch panel paintings of the first half of the seventeenth century, though pure oil-bound layers also occur.

Table 5.1  List of paintings examined

- Michael Sweerts, *Draughts Players*, (Mauritshuis, inv. no. 1121), 1652, oil on canvas, 48 x 38 cm
- Roelandt Savery, *Orpheus enchanting the Animals with his Music*, (Mauritshuis, inv. no. 157), 1627, oil on oak panel, 62 x 131.5 cm
- Aert van der Neer, *River Landscape*, (Mauritshuis, inv. nr. 912), mid-1650s, oil on oak panel, 44.8 x 63 cm
- Jan van Goyen, *Dilapidated Farmhouse with Peasants*, (Mauritshuis, inv. no. 1081), 1631, oil on oak panel, 40 x 45 cm
- Jan van Goyen, *River View*, c. 1644-48, (Mauritshuis, inv. no. 759), oil on oak panel, 37 x 64 cm

---

2 Technical investigations of the paintings were carried out together with the conservators in the Mauritshuis 2002-2007, and with the conservators involved in the restoration of the Trippenhuis ceilings 2006-2007.

3 This build-up of ground layers is based on cross-sectional and elemental analyses of many panel paintings from this period in the collection of the Mauritshuis. This is proving to be in accordance with recipes for grounds from seventeenth-century documentary sources [Witlox and Carlyle 2005].
Darkening as a result of increased transparency in 17th century oil paintings

- Jan Steen, *Dancing Peasants at an Inn*, (Mauritshuis, inv. no. 553), c.1644-48, oil on oak panel, 40 x 58 cm

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

**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). Cross-sections prepared in the Conservation Studio of the Mauritshuis were made using Easy Sections (VWFecit, England) using Poly-pol PS230 polyester mounting resin with M.E.K.-peroxide harder (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 inc., Wilton, Iowa, USA).

**INSTRUMENTATION**

A Leica DMRX microscope was used to study the layer structure of the cross-sections. Specular reflection FTIR imaging of the cross-sections was done using the Biorad FTS Stingray 6000 system, with a 64x64 pixels MCT Focal Plane Array detector. Analytical results of the FTIR imaging measurements are displayed as infrared spectra and false color or gray-scale distribution images of selected absorption bands. The cross-sections were then carbon coated before examination in a FEI XL30 SFEG high vacuum scanning electron microscope (SEM). Elemental analyses (EDX) of the samples were carried out with the energy dispersive x-ray detector from EDAX attached to the SEM. Backscatter electron images of the cross-sections and information on elemental composition were obtained. Furthermore, isolated samples were analyzed using DTMS and/or single-point transmission FTIR to characterize the binding media. DTMS analyses were carried out using a JEOL JMS-SX/SX102A 4-sector double-focusing mass spectrometer. Selected sample material was applied onto a Graseby Specac P/N diamond cell to perform single-point transmission FTIR measurements using a Biorad FTS-6000 FTIR spectrometer extended with a Biorad UMA-500 IR Microscope. See more technical and instrumental details in the experimental section in Chapter 1.

---

4 Sample preparation was carried out by the Conservation Studio Mauritshuis.
RESULTS

A. INCREASED TRANSPARENCY AND DARKENING OF LEAD-TIN YELLOW PAINTS

MICHAEL SWEERTS ‘DRAUGHTS PLAYERS’ 1652 (MH 1121)

In Sweerts’ *Draughts Players*, the yellow stocking of the right figure demonstrates an unusual patchiness owing to increased transparency of the paint (Fig. 5.1). The stocking is painted over a dark, almost black underlayer that is now shimmering through the partly transparent surface paint. A cross-section of a paint sample from a similar area painted with the same pigment, the yellow tassel of the stool on the left, shows the upper paint layer to contain lead-tin yellow Pb₂SnO₄ mixed with a little ultramarine and orange-colored earth pigment (Table 5.2; Fig. 5.2). In this sample, the reddish-brown earth ground, demonstrated in other cross-sections from the painting, are missing. Light microscopic and SEM studies of the yellow layer demonstrate that the original lead-tin yellow paint consists of various heterogeneous phases. A large cluster of lead-tin yellow particles, visible at the left in the cross-section, as well as a few particles here and there throughout the layer (Fig. 5.2), exhibit the characteristic ochreish color in UV

---

5 This was noted during restoration of the painting carried out by Petria Noble in 2001-2002.
Darkening as a result of increased transparency in 17th century oil paintings

and strong scattering in the backscattered electron images. Accordingly the EDX maps of these areas demonstrate the elements lead and tin (Fig. 5.2). For the most part, the layer, however, looks far from the normal homogenous paint layer consisting of opaque yellow particles. Instead the light microscopic image reveals many transparent regions that correspond to gray amorphous areas in the SEM backscatter mode having a lower lead density compared to the particles of intact lead-tin yellow having a high lead density.

---

6 Lead-tin yellow type I was established in a sample from the yellow stocking using X-ray powder diffraction. Analysis carried out by Arie Wallert, Rijksmuseum Amsterdam 2002 at the ICN [Wallert and De Ridder 2002: 45, note 32].
The affected layer also appears to have expanded. It is notable that no tin is detected in these gray areas, but rather only lead and large amounts of carbon (Fig. 5.2). The FTIR imaging data demonstrate dispersed lead soaps throughout the paint layer by the prominent absorption bands at \( c.1509 \text{ cm}^{-1} \) and \( c.1403 \text{ cm}^{-1} \) attributable to the lead carboxylate group, \( \nu_\text{s}(\text{COO}) \) and \( \nu_\text{a}(\text{COO}) \) (Fig. 5.2). Absorption peaks for the C-H bonds, typical of the aliphatic chain of the carboxylate, at \( c.2941 \text{ cm}^{-1} \nu_\text{a}(\text{CH}_2) \) and \( c.2854 \text{ cm}^{-1} \nu_\text{s}(\text{CH}_2) \) are also demonstrated. In earlier published studies of lead soap, protrusions/aggregates in lead-tin yellow paints, it was postulated that the excess lead oxide in the lead-tin yellow pigment, a lead-tin oxide (lead ortho-stannate), reacts with fatty acids released during drying/ageing of the oil medium to form lead carboxylates [Boon et al. 2004; see also section on lead-tin yellow in Chapter 2]. The selective reaction of lead with the free fatty acids can be explained by the fact that the tin(IV) oxide component is very stable and does not form carboxylates. The spongy, porous structure of the lead-tin yellow pigment that makes this pigment highly oil absorbent\(^7\), explains the source of fatty acids available for saponification.

**Conclusion**

It can be concluded that the original lead-tin yellow paint is converted to a partly transparent metal soap-rich layer leaving some residual pigment. The reduced amount of lead-tin yellow particles explains the loss of scattering in the upper paint layer that allows for the dark underpaint of the stocking to shine through. The partial saponification of the paint also allows the other colored pigments present in the yellow paint layer, the blue (ultramarine) and the orange (earth pigment), to play a more role in the color perception of the transparent areas. The loss of scattering and loss of the yellow component in the paint have led to a darkened appearance of the paint.

**DARKENING OF MEDIUM BROWN AND GRAY TONES**

*Roelandt Savery ‘Orpheus Enchanting the Animals with his Music’ 1627 (MH 157)*

The extreme darkening of the medium brown paint layers in a landscape by Roelandt Savery - *Orpheus Enchanting the Animals with his Music*,\(^8\) that cover a large portion of the picture, has resulted in strong visual distortion of the original light and dark contrasts and severe loss of detail (Fig. 5.3). The animals, birds and tiny details depicted on top of this layer are now barely visible to the naked eye. A cross-section of a paint sample from the distant landscape in the upper left shows the brown layer as intermediate layer below the green top layer of the landscape (Table 5.2; Fig. 5.4). The brown paint is composed of lead white, fine carbon black and red and yellow ochres. The translucent areas in this

---

\(^7\) During one of the pigment meetings in 2003 held at FOM-AMOLF, Leslie Carlyle pointed out that the oil absorption by lead-tin yellow is 25%, compared to 5% by lead white.

\(^8\) Treated by Sabrina Meloni during internship in the Mauritshuis (SRAL intern 2002-2003) and documented in her final thesis [Meloni 2003].
layer exhibit a strong fluorescence in UV. The brown layer is applied directly on top of the priming layers, a chalk ground followed by a thin gray imprimatura consisting of lead white, fine lamp black and a few red (earth?) particles. The backscattered electron images reveal gray amorphous areas in much of the brown layer, apart from some (residual) lead white pigment (Fig. 5.4). In these areas, only lead and a high carbon content are detected. The EDX map of lead shows dispersed lead throughout the whole brown intermediate layer (Fig. 5.4). It seems that most of the original lead white in this layer has dissolved and converted to lead soaps. In addition, several small protrusion-like masses are situated in the brown layer (in the right part). These occluded masses show fine horizontal striations correlating with higher lead densities that can be interpreted as mineralized lead soaps. The presence of lead soaps is supported by the FTIR imaging data. The FTIR image of the 1510 cm\(^{-1}\) absorption band, typical of lead carboxylate \(\nu_2^{\text{COO}}\), demonstrates a high intensity band corresponding to the middle, dark brown layer (Fig. 5.4).

Another cross-section from the dark background tells a similar story (Table 5.2). Here, the dark paint layer is the upper, exposed layer. The priming layers are missing in this sample. The UV image shows many fluorescent zones in the dark paint layer. The backscattered electron images, again, demonstrate a severely saponified layer. A few large, coarse particles of lead white are still intact, but the main part of the layer has a (grayer) less dense and more amorphous appearance. Here it is postulated that the small particles of lead white are more reactive towards the oil medium and therefore dissolve more easily and quickly than the larger particles. In addition, a thin lead-containing film (max. 2-3 \(\mu\)m) has deposited at the surface of the layer that probably accounts for the blanched/whitened appearance of this dark paint area noticed after varnish removal. Diffusion of lead soaps from the brown layer towards the surface, comparable to some of the case studies discussed in the previous chapter (Chapter 4), seems to have taken place. The presence of a minor trace of sulfur in the surface crust, in addition to lead and carbon, suggests that some lead sulfate has formed, presumably as a result of interaction of the lead carboxylates with sulfur compounds from the atmosphere. This would also explain the peak present at \(m/z\) 64 (SO\(_2\)) and small peak at \(m/z\) 48 (SO) in the DTMS spectra of the brown surface paint, indicative of sulfur dioxide.

Binding medium analysis of isolated samples of the brown surface layer using DTMS demonstrates high amounts of oil components. Mass peaks detected are \(m/z\) 256 and 284 typical of palmitic and stearic acid, and \(m/z\) 152 from a fragmentation ion of azelaic acid (C9 diacid).\(^9\) Their occurrence in the higher temperature regions in the chromato/thermogram (scans 78-88) indicates that part of the fatty acid fraction is metal-bound and not in free form [Keune 2005b], which is in accordance with the SEM and FTIR data. The inorganic fraction (scans 81-130) shows the isotope pattern for lead at \(m/z\) 206-208, and some sulfur at \(m/z\) 64 (see discussion above). DTMS also provides information about the presence of the cross-linked oil network fraction of the paint sample. In the higher temperature region (scans 78-88), the typical peak pattern

\(\text{In addition, the spectra contain longer chain fatty acids, C20FA-C26FA, at } m/z 312-396.\)
Chapter 5

of the pyrolysis products of the oil paint network is discernible with mainly aromatic components (e.g. \(m/z\) 91, 105).\(^{10}\)

**Conclusion**

The analyses reveal an oil medium-rich, saponified layer. Nearly all the lead white in the brown layer has reacted away into soaps: the lead soaps are dispersed throughout the layer. Brown- and gray-toned paints typically contain black carbonized products and earth pigments that are known to be highly oil-absorbent. It is thought that they have supplied the fatty acids required for the conversion of the lead white pigment in the layer into lead soaps. Originally, a lighter and cooler tone must have been meant. The loss of the white component in this layer makes the brown/gray paint appear much darker and warmer than originally intended. As a result of the darkening effect, the animals and other details painted on top of this layer in the foreground are now only barely visible. Moreover, the saponification/loss of opacity of the lead white has strongly influenced

---

\(^{10}\) Furthermore, traces of pine resin (DHA at \(m/z\) 239, 287, 300 and OXO-DHA at \(m/z\) 253, 314, 315, 330) and mastic (at \(m/z\) 163 and 400-450 region) were detected, that are likely to be residues of old varnish.
Fig. 5.4 Light microscopic images of cross-section from distant landscape (upper row), with corresponding FTIR images, EDX maps and SEM backscattered electron images. The saponified brown layer is the intermediate layer below the (green) top layer of the landscape. The white bands in the FTIR maps represent areas of high intensity.
the color balance of the whole picture: the dark foreground now strongly contrasts with the light, bright blue sky, unintentionally creating a kind of dramatic chiaroscuro effect.\footnote{From their composition, these middle brown- and gray-toned oil paints are very prone to darkening. A similar darkening process due to saponification of the lead white component may be responsible for the now dark areas in Raphael’s Transfiguration of Christ [Van Eikema Hommes 2004b], as well as in many other oil paintings.}

\section*{C. SELECTIVE DARKENING OF GROUND AND PAINT LAYERS ON THE WOOD GRAIN}

\textbf{AERT VAN DER NEER ‘RIVER LANDSCAPE’ MID-1650S (MH 912)}

Loss of opacity is also observed associated with the wood grain on the radial surface of panel paintings creating disturbingly dark stippled lines that have often been interpreted as abrasion. In a panel painting by Aert van der Neer, dated mid-1650s - River Landscape-, many areas in the sky were found to be disturbed by dark lines that are associated with the wood grain in some way.\footnote{The localized darkening in this picture was investigated together with Petria Noble 2002-2006. Treatment of the picture was carried out by Alice Mohan (Maîtrise de Sciences et Techniques (M.S.T.), University Paris I Panthéon-Sorbonne) during her three-month internship in the Mauritshuis 2002. The same phenomenon, though less visible, is present in Aert van der Neer’s River Landscape at Sunset, c.1650, (Mauritshuis, inv. no. 913).} Although they were also present in the darker areas of the picture, they were most disfiguring in the bright peach-colored sky. These streaks, which were found to correspond to the porous early wood on the radial surface, have become selectively more transparent and darker in tone, in contrast with areas of intact opaque paint on the late wood (Fig. 5.5). Examination with the stereomicroscope revealed that the streaks are formed in the underlying lead white-containing pinkish brown \textit{imprimatura} that shimmers through the very thin sky paint or has become exposed as a result of loss of the sky layer.

In several cross-sections from the sky, three layers are present (Table 5.2): a chalk ground of variable thickness, a pinkish brown \textit{imprimatura} (10-20 µm) and a single thin pinkish-grey sky layer (approx. 10 µm), consisting of lead white with the addition of a little vermilion, umber and glass (also carbon black in the grayer areas of the sky). In two cross-sections from the darkened lines, the \textit{imprimatura}, which is essentially composed of large particles of lead white and a few large rounded particles of a relatively transparent red-brown umber (EDX: Fe, Mn, Si, Al, (Mg, K)), appears unusually transparent. Furthermore, small reddish umber particles are observed in these transparent areas (more Fe-rich than the browner umber particles) in close proximity to the brown umber particles. It is notable that in the samples from darkened areas a thick chalk ground is present (up to 60 µm thick), while in unaffected areas the chalk layer is thin or barely present. This difference in thickness of the ground is also apparent on the end grain (transverse sections) of the panels when viewed with the stereomicroscope. The ground fills the large pores of the vertical parenchyma cells of the early wood, which are huge in comparison with the smaller pores in the dense late wood (Fig. 5.6). Hence, we conclude that where the wood is porous (the early wood), the ground is thick because
it penetrated the cells opened by planning and sanding of the panel; where the wood is dense (the late wood), hardly any ground is present. The deep channels of the early wood can be clearly discerned on the back of the panel (Fig. 5.6). It is primarily these areas that become filled with ground during preparation of the panel. Dendrochronology concluded that the oak panel is of Baltic origin with an earliest felling date of about 1642.13

Imaging FTIR analysis of the cross-sections confirmed metal soap formation in the transparent regions of the *imprimatura* by strong absorption in the 1510-20 cm\(^{-1}\) region that is characteristic for lead carboxylates. Detailed information on the morphology of the affected layer was demonstrated with SEM. In Figs. 5.5 and 5.7, the SEM backscattered electron images of cross-sections from the intact and darkened areas in the sky are displayed. The difference in the morphology and distribution of the lead white is striking. The *imprimatura* in the intact sample shows a lead white-rich layer with a broad distribution of both fine and coarse particles typical of seventeenth-century Dutch stack-processed lead white. In contrast, in samples from darkened areas, the fine lead white particles appear to have reacted away forming large transparent regions throughout the layer leaving only the largest particles intact. This corresponds to the observation of large lead white particles in a transparent brownish matrix in these areas on the surface of the painting. Compared to normal, dense, intact lead white particles, the saponified areas appear less dense, grayed and amorphous in the backscatter images due to their higher organic content. Some intact lead white particles, however, do demonstrate grayed peripheries, corresponding to transparent perimeters seen in normal light microscope images, that indicate a progressive transformation into lead soaps. It is notable that the altered *imprimatura* is much thicker than non-affected *imprimatura* due to the larger volume of the saponified lead white particles and that the sky layer is partially missing in samples from darkened areas. EDX analysis confirmed the lead involved in soap formation.

It is also noted that the chalk ground appears particularly porous. Binding medium analysis carried out with DTMS on an isolated sample of the chalk ground -from an area in the sky at centre right- suggests that the highly porous glue-bound ground has absorbed oil from the layer(s) above. In the mass spectra the signals for animal glue are almost obscured by the large amounts of oil derived components, the monocarboxylic and dicarboxylic fatty acids.14 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). Only a small part of the fatty acids seems to be bound to the oil network, since the main fraction is released from the probe at low temperature (scans 25-40) indicating that they must be present in the free form [Keune 2005b]. The DTMS spectra also give evidence for the presence of chalk because of the release of \(\text{CO}_2\) (\(m/z\) 44) detected at high scan numbers (scans 92-107) that is associated with the carbonate group from the chalk.

---

13 Dendrochronology by Peter Klein, University of Hamburg, 2002.
14 Resin components, pine resin and dammar, identified with DTMS in the chalk ground, were probably introduced during past cleaning and varnishing. This indicates how absorbent/porous the chalk ground is.
Fig. 5.5 Aert van der Neer, *River Landscape*, c.1650 (Mauritshuis, inv. no. 912). Overall (inset) and detail of dark streaks in centre right sky (*upper row*); microscope detail (*center left*); light microscopic image of cross-section from dark streak (*center right*); SEM backscatter image of cross-section (912x10) from unaffected grey sky at upper right (*lower left*) and SEM backscatter image of cross-section (912x11) from dark streak immediately next to intact sample (sky layer is missing from this sample) (*lower right*).
Darkening as a result of increased transparency in 17th century oil paintings

Fig. 5.6 Microscope detail of reverse of Aert van der Neer showing deep channels of the oak panel (left). Detail of the transverse section (end grain) showing chalk ground that preferentially fills the large cells of early wood (right).

Fig. 5.7 SEM backscattered electron image of cross-section of dark streak (912x11) in Fig. 5.5 enlarged showing dissolution and saponification of lead white pigment in *imprimatura*. 
Chapter 5

Conclusion

In this case, the darkened *imprimatura* either shines through the thin translucent upper layer or is exposed where it has expanded causing the upper layer to flake off (expansion is a characteristic of lead soaps borne out of previous investigations of metal soap aggregates). Not only is the selective darkening in the *imprimatura* related to the high degree of saponification of the lead white, but it is also related to the loss/lack of reflectivity of the chalk ground by absorption of oil from the paint layers. The presence of oil in the chalk ground, as detected with DTMS, may explain the source of free fatty acids required for the transformation of lead white into lead soaps.

During the recent treatment, careful retouching was necessary to hide the lines in order that the picture could be displayed in the galleries; after retouching the painting is closer to its original appearance.

**Jan van Goyen ‘Dilapidated Farmhouse with Peasants’ 1631 (MH 1081) and ‘River View’ c. 1644-48 (MH 759)**

Investigations of two similarly affected panel paintings by Jan van Goyen - *Dilapidated Farmhouse with Peasants*, dated 1631, and *River View* from c. 1644-1648, show consistent results. In these essentially tonal paintings, not only are disturbing lines visible over the entire surface, but the loss of a reflective surface layer permits the shining through of the darkened underlying layers (and the panel) resulting in a loss of detail and distortion of color, particularly in the thinly painted and damaged areas such as the skies (Figs. 5.8 and 5.9). As a result, the careful attention to the creation of the atmospheric quality of light is now largely lost. While these alterations are clearly visible with the naked eye, the cause of the darkening effect is much more difficult to distinguish under the stereomicroscope. In both cases, microscopic examination revealed selective flaking and cracking of the surface paint exposing the underlying *imprimatura* along the areas associated with the early wood of the wooden panel.

It is in the study of paint cross-sections from affected and non-affected paint layers that the cause of the darkening phenomenon is found (Table 5.2). In the sky areas from both paintings three layers are present: a chalk ground (up to 60 µm), a light lead white-containing *imprimatura* (10-20 µm) with the addition of a little carbon black or some umber as the coloring component, and a single very thin sky layer consisting mainly of lead white and a little smalt (10-15 µm). Comparable with the Aert van der Neer, in both samples from affected areas a thick chalk ground is present while in unaffected areas, the chalk ground is barely present. Here again, the difference in the thickness of the ground is found to be related to the uneven structure of the wood grain: in the denser late wood there is hardly any ground present whereas in the porous early wood the ground is thick filling the cells opened by the planing of the wood panel. The *imprimatura* in both Van Goyens differs slightly in composition from that in the Aert van der Neer painting. Here, chalk has been added to the lead white, suggesting

---

15 The localized darkening in these pictures was investigated together with Petria Noble 2002-2006, as part of the Open Laboratory agreement between Mauritshuis and FOM-AMOLF.
a slightly translucent effect may have been aimed for, or alternatively the use of the cheaper variety of lootwit, rather than the pure form of schulpwit [Van de Graaf 1958, pp. 34-35]. The sky layer manifests itself as a very compact layer containing fine and some coarser particles of lead white. Here, the sparsely distributed smalt is mostly intact and appears grayish-blue in cross-section. In comparison, cross-sections from the affected areas demonstrate only partial remains of the sky layer (Fig. 5.8), confirming the surface observation that the sky paint in these areas has largely flaked off revealing the imprimatura that has become selectively transparent and darker in appearance.

In SEM backscatter images of the cross-sections from the affected areas in both paintings, it is remarkable that the majority of original lead white in the imprimatura layers has converted to lead soaps (Figs. 5.8 and 5.9). The intact particulate lead white pigment particles show strong scattering and appear white, while the less dense (grayer) amorphous areas point to saponified areas. In the gray amorphous areas a lower concentration of lead and higher carbon content were detected as compared to the intact lead white where a higher lead and lower carbon content was demonstrated. These concentration differences are also illustrated in the EDX map of lead. The low-scattering (dark) rounded areas are the chalk particles, which are also demonstrated in the calcium map. This is in contrast to cross-sections from unaffected areas, where much more

---

**Fig. 5.10** DTMS analysis of chalk ground from Jan van Goyen, *River View* (Mauritshuis, inv. no. 759). A) total ion current (TIC) diagram; B) summed mass spectra of low temperature event (scans 10-50) showing free fatty acids, mainly \textit{m/z} 256 palmitic acid and \textit{m/z} 284 stearic acid, and C) mass chromatograms of ions from azelaic acid (\textit{m/z} 152), general marker for saturated fatty acids (\textit{m/z} 129), palmitic acid (\textit{m/z} 256), polymeric network (\textit{m/z} 91), animal glue (\textit{m/z} 117, 154) and chalk (\textit{m/z} 44).
Fig. 5.8 Jan van Goyen, River View, c. 1644-1648 (Mauritshuis, inv. no. 759). Overall and detail of dark lines in upper left sky (center left); microscope detail (center right); SEM backscatter image of cross-section (759x01) from darkened sky showing the sky layer has largely flaked off (lower left) and SEM backscatter image of cross-section (759x02) from darkened line in sail of boat (lower right).
Fig. 5.9 Jan van Goyen, *Dilapidated Farmhouse with Peasants*, 1631 (Mauritshuis, inv. no. 1081). Overall and detail from upper left sky showing disturbing horizontal lines (*center left*); microscope detail (*center right*); SEM backscatter image of cross-section (1081x03) from unaffected grey sky (*lower left*) and SEM backscatter of cross-section (1081x01) from darkened area in grey sky (*lower right*) (same scaling).
intact lead white surrounds the chalk particles, and corresponds to the light microscopic images, where this layer also appears more opaque in the samples from the intact areas.

Binding medium analysis was also carried out on isolated samples of the ground from each painting taken at the edges of the panels. The organic components, detected using DTMS analysis, are similar to the chalk ground in the Aert van der Neer. In both Van Goyens, markers for animal glue (m/z 70 and 154) and chalk (CO₂ event at high scan numbers) are present, as well as free monocarboxylic and dicarboxylic fatty acids associated with oil (Fig. 5.10). The DTMS results confirm the presence of a fatty acid source that is needed for the conversion of lead white into soaps.

Conclusion
Here again, the thickness of the ground in relation to the panel’s wood structure corresponds with different degrees of lead soap formation in the imprimatura. It can be concluded that the striped pattern of darkened lines created in the affected areas is a result of the surface paint flaking off in areas corresponding to the early wood of the oak panel whereby the darkened imprimatura (and support) has become exposed. For both Van Goyens, the dark lines are so disturbing that the pictures can no longer be displayed in the galleries. Given that the stripiness covers most of the surface of the paintings introduces aesthetic and ethical issues. It remains questionable whether one should consider retouching or overpainting such large areas.

Jan Steen ‘dancing peasants at an inn’ c.1644-48 (MH 553)

In this early panel painting by Jan Steen, darkened lines associated with the wood grain/uneven wood structure are visible over the entire surface, but are most disturbing in the sky areas, and are also notable in the foreground and in the figures (Fig. 5.11). Prior to the picture’s recent treatment, numerous darkened lines were found to be covered with old, now discolored, retouching.

Cross-sections were taken from a darkened line in the sky and from an intact (blue) area for comparison. The cross-section from the darkened area also includes two layers of blue overpaint that comprises modern cobalt blue pigment (a cobalt aluminum oxide, CoO·Al₂O₃). Unfortunately, the ground and imprimatura layers are missing in this sample, since they crumbled during the sampling process. Like the other paintings under examination, this darkened area clearly correlates to the porous channels of the early wood that is filled with a thick layer of ground material. This is visible on the surface, in other darkened areas, where the surface paint is lost and the chalk ground that appears light brownish in color has become exposed. The cross-section from the intact blue area (see Table 5.2) shows the complete paint layer build-up: a chalk ground (up to 40 µm), a very thin light gray imprimatura (c.5 µm) and a single gray-blue sky

---

16 Ground samples in these paintings were also found to be contaminated with resin components associated with the varnish layers: dammar, pine resin and a modern synthetic methyl ketone resin (AW2 BASF Methylcyclohexanone).

17 Analysis by FTIR of dark material collected from the deep porous channels of the early wood mainly showed peaks for cellulose from the wood, in addition to a little chalk. This implies that local shimmering of the panel through the upper paint layers that have become increasingly transparent also plays a role in the selective darkening.
layer (c.15 µm) consisting of lead white and smalt and a few black and red particles. The *imprimatura* is composed of rounded particles of chalk, fine and coarser lead white and a little carbon black and appears rather opaque in this cross-section. The difference in the appearance of the sky layer in the light microscopic images between the affected and unaffected is striking, the darkened layer consisting only of a few large lead white particles in a transparent brown matrix. This was also noted on the surface of the painting in the darkened areas. The unaffected sky layer, in contrast, demonstrates an opaque layer, in which both large and small lead white and grayish angular particles of smalt are discernable. This difference between the affected and unaffected is also reflected in the SEM backscatter images of these layers. In the image of the unaffected area, a broad distribution of particularly fine lead white with some coarse particles is demonstrated, whereas in the cross-sections from the darkened area all the fine lead white particles have reacted away leaving only a few coarse particles (Fig. 5.11). The less dense, (gray) amorphous areas in the backscatter image, prominent throughout the whole sky layer, indicate the transformation to lead soaps. In both cross-sections, the low potassium concentrations inside the smalt particles (<1 wt %, measured by EDX) indicate that the smalt is almost completely discolored. Here, the paint matrix clearly has a strong influence on the color perception. When the discolored smalt is situated in a highly reflecting matrix, such as the fine lead white, it still appears gray-blue on the paint surface. In the transparent brown matrix, however, the pale blue color is completely lost.

A darkened line in the brown foreground, next to the tree trunk in the lower foreground, was also sampled. Here the cross-section reveals an incomplete chalk ground (c.10 µm), since again part of it crumbled during sampling. In this sample, the *imprimatura* is barely present. The semi-transparent dark brown paint layer (c.15 µm) comprises azurite, smalt, chalk, dispersed lead and red earth. In comparison, a sample from a non-darkened area, just next to the darkened line, reveals a light-gray underlying *imprimatura* (c.10 µm) containing some rather coarse lead white, followed by the same dark brown upper layer (c.20 µm). Here, the light *imprimatura* reflects some of the light and shimmers through the upper layer, creating a lighter appearance on the surface compared to the darkened line where the *imprimatura* is barely present.

**Conclusion**

The darkened lines in the painting can be explained by saponification of the lead white particles in the surface layers and very thinly applied *imprimatura*. The resulting loss of reflectivity of the paint and *imprimatura*, combined with the darkened chalk ground in these areas (from absorption of the oil from the *imprimatura*), permits the shining through of the panel in these areas. The results show that saponification of lead white is not restricted to the *imprimatura*, but can also affect lead white-containing surface layers, in this case, selective areas of the sky, as determined by the chalk ground that fills the uneven oak wood structure.
Chapter 5

Fig. 5.11 Jan Steen, Dancing Peasants at an Inn, c. 1646-1648 (Mauritshuis, inv. no. 553). Overall and detail of dark streaks upper left sky (center left); microscope detail from figure in foreground (center right); SEM backscatter image of cross-section (553x04) from unaffected blue sky (lower left) and SEM backscatter image of cross-section (553x01) from overpainted dark line in sky (lower right) (same scaling).
Fig. 5.12 Trippenhuis, painted ceiling N1, 1660-62 with detail of the discolored sky; detail of backscattered electron image showing saponification of the lead white, as seen by the gray halos (center right); light microscopic image of cross-section from discolored sky N1 (lower left) with corresponding SEM backscatter image (lower right). The browish areas in the cross-section correspond with low scattering, saponified areas in the SEM.
D. INCREASED TRANSPARENCY AND DARKENING (BROWNING) OF BLUE PAINTS CONTAINING SMALLT AND LEAD WHITE

TRIPPENHUIS’ PAINTED CEILINGS WITH HUNTING SCENES WITH SKIES AND BIRDS’ 1660-62

The ceilings in the corridors and stairwells of the Trippenhuis, a palatial house (actually a double house) on the Kloveniersburgwal in Amsterdam built for the two brothers Louys and Hendrick Trip by the architect Justus Vingboons between 1660 and 1662, are richly decorated depicting hunting scenes with painted skies with birds. For centuries, the painted ceilings had been covered by many layers of monochrome overpainting, but these were removed in two phases, in the southern house in the 1980s and in the northern house in the early 1990s, to expose the original decoration schemes. Large areas of the originally blue skies now appear discolored and have a brownish, patchy appearance (Fig. 5.12). We examined about 15 cross-sections from the skies, from discolored areas as well as from areas that still appear blue, using light microscopy and SEM-EDX.18

The cross-sections show great similarities in the layer structures: a chalk ground, followed by a light lead white-containing preparation layer, and one or two applications of blue paint mixtures of lead white and smalt (Table 5.2). It seems that the brownish appearance of the paint is only partly due to degradation of the blue smalt particles. Although they are clearly in the process of discoloration, there are still many blue or bluish particles (with high K levels) discernable in cross-sections from both blue and discolored/browned areas. We infer from the cross-sections that saponification of the lead white pigment is mainly responsible for the observed color differences on the paint surface. In general, the cross-sections from the blue areas reveal higher densities of reflecting lead white particles, while the smalt layers from brownish areas have become transparent in places throughout the layer. The transparent areas in the light microscopic images correspond to less dense (grayer) areas in the SEM backscatter images showing amorphous, cloudy morphologies that point to saponified areas. The EDX maps of lead confirm the presence of lead in these areas where it is not associated with distinct lead white pigment particles. It is noted that the smalt particles that are situated in these brownish transparent areas are hardly perceptible in the light microscopic images and appear almost transparent (Fig. 5.12). Dissolution of the lead white reduces the number of internal light reflections in the paint decreasing the hiding power. The light penetrates deeper. This also implies that less blue light is bounced back by the smalt particles, but instead is absorbed by the brownish matrix. A similar optical effect was noticed in the cross-sections from the sky in the Steen (see previous example). The visual impact of the darkening effect is also found stronger in the thinly painted areas, like the interstices of the brushwork as compared to the raised areas.

18 The ceilings are currently being restored by Edwin Verweij | Verweij Office for Architectural Paint Research and Conservation Amsterdam and Ruth Jongsma | Bureau voor Kleuronderzoek en Restauratie Amsterdam.
Conclusion
Saponification of the lead white is considered the main cause for the increased transparency and consequent darkening/browning of the blue sky paints (composed of smalt mixed with lead white) that affect large areas of the Trippenhuis ceilings. The loss of scattering material in the blue paint not only makes the paint more transparent but also reduces the blue tone/hiding power of the smalt. Unlike the Steen, the darkening of the sky paints in the Trippenhuis cannot be associated with the wood structure/grain. Why some areas in the skies are more affected by degradation than others largely seems to depend on small local differences in climate conditions (moisture, pH and temperature) within the paints. Furthermore, such handmade paints always show a certain degree of inhomogeneity. Even though the sky paints show very similar compositions and layer structures, there are always small differences in e.g. particle size, pigment volume concentration, support, and thickness of the preparation layers that may further explain the differences in degree/level of degradation.

Discussion
Chemical and Optical Changes
The reduction in opacity (i.e. increase in transparency) causing the darkening observed on the surface of the paintings presented can be explained by (partial) conversion of the lead white or lead-tin yellow pigment to metal soaps. From observation of the paint surface and the cross-sections, and as previously noted, it would seem that the smaller lead white particles first react away, leaving only the larger particles that are also clearly in the process of transforming into lead soaps. The opaqueness of lead white in oil is directly correlated to its light scattering ability. The transformation of lead white pigment particles to amorphous lead soaps will lower the light scattering ability and, instead, causes the light to penetrate deeper into the paint resulting in a darker appearance (Fig. 5.13). While a RI value for lead soaps has been assumed between that of the oil and the pigment [Robinet and Corbeil 2003: 24], recent measurement indicates a value close to that of the oil, 1.50-1.55. The gradual transformation of the lead white (or lead-tin yellow) particles to lead soaps significantly lowers the difference in refractive index between the binding medium and the pigment, leading to an increase in transparency. Moreover, any partially converted particles of lead white effectively become embedded in a high RI medium (the lead soaps) and thus appear transparent.

The optical effects caused by saponification of the lead white or lead-tin yellow can be significant, especially in the case of pigment mixtures or the presence of a dark underlayer. As with the yellow stockings in the Sweerts, the darkening effect observed on the surface is enhanced by the dark, almost black underlayer that shimmers through the yellow layer that has become increasingly transparent. In the case of increased transparency and darkening of ground layers, as with the phenomenon of localized

---

19 Measurement carried out on synthesized lead palmitate at room temperature. Personal communication, Yoshiko Shimadzu, ICN, Amsterdam, October 2007.
### Table 5.2  Increased transparency and darkening: summary of samples and analysis

<table>
<thead>
<tr>
<th>Artist, title, date, support</th>
<th>Sample location</th>
<th>Paint build-up</th>
<th>Paint defect</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Increased transparency in lead-tin yellow paints</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Michiel Sweerts <em>Draughts Players (MH 1121)</em></td>
<td>Yellow tassel of stool, at left 1121x18</td>
<td>1. yellowish upper layer: lead-tin yellow, orange earth pigment, ultramarine (ground missing)</td>
<td>Saponification of lead-tin yellow in yellowish top layer resulting in a patchy, darkened appearance of the paint surface</td>
<td>LM FTIRima SEM</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Darkening of medium brown and gray tones</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Roelandt Savery <em>Orpheus Enchanting the Animals with his Music (MH157)</em></td>
<td>Green landscape over brown background 157x36</td>
<td>1. chalk ground 4. green landscape layer: copper pigment, chalk, silicates? 3. brown background layer: lead white, carbon black, earth pigments 2. gray <strong>imprimatura</strong>: lead white, fine lamp black, little red</td>
<td>Saponification of lead white in medium brown background layer that has led to darkening of the layer</td>
<td>LM FTIRima SEM DTMS</td>
</tr>
<tr>
<td></td>
<td>Dark background 157x14</td>
<td>1. brown upper layer: lead white, carbon black, earth pigments (priming layers missing)</td>
<td>idem</td>
<td>idem</td>
</tr>
<tr>
<td><strong>Selective darkening on the wood grain</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aert van der Neer <em>River Landscape (MH 912)</em></td>
<td>Pink sky 912x05 (darkened) 912x10 (intact) 912x11 (darkened)</td>
<td>1. chalk ground (up to 60 µm thick) 3. pinkish gray sky layer: lead white, little vermilion, umber, glass + carbon black in the gray areas of the sky (c.10 µm) 2. pinkish brown <strong>imprimatura</strong>: lead white, umber (10-20 µm)</td>
<td>Darkening due to saponification of lead white in <strong>imprimatura</strong></td>
<td>LM FTIR SEM DTMS (ground)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jan van Goyen <em>Dilapidated Farmhouse with Peasants (MH 1081)</em></td>
<td>Gray-blue sky 1081x01 (darkened) 1081x02 (darkened) 1081x03 (intact)</td>
<td>1. chalk ground (up to 60 µm) 2. light-gray <strong>imprimatura</strong>: lead white, chalk, little carbon black (10-20 µm) 3. gray-blue sky layer: lead white, (intact) smalt (10-15 µm)</td>
<td>Darkening due to saponification of lead white in <strong>imprimatura</strong></td>
<td>LM SEM DTMS FTIR (ground)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jan van Goyen <em>River View (MH 759)</em></td>
<td>Gray-blue sky 759x01 (darkened) 759x02 (darkened) 759x03 (darkened)</td>
<td>1. chalk ground (up to 60 µm) 2. light-beige <strong>imprimatura</strong>: lead white, chalk, little umber (10-20 µm) 3. gray-blue sky layer: lead white, (intact) smalt (10-15 µm)</td>
<td>Darkening due to saponification of lead white in <strong>imprimatura</strong></td>
<td>LM SEM DTMS (ground)</td>
</tr>
</tbody>
</table>
Darkening as a result of increased transparency in 17th century oil paintings

Darkening on the wood grain, the thinner or translucent areas in the paintings, usually the sky areas, are affected worst since they allow the darkened underlayers to shine through. The loss of the white pigment in medium to dark paint layers as a result of saponification may also lead to color changes that can have a great visual impact on paintings, the dark areas of the painting becoming much darker than originally intended. This was seen for example in the landscape by Savery, where darkening of the brown and gray medium tones in the foreground has resulted in a noticeable distortion of the original light/dark contrasts: the animals disappear in the foreground, and the dark foreground stands out too strongly against the light, blue sky. Particularly interesting is also the effect of increased transparency of the surrounding medium on the hiding power and color intensity of other pigments in the layer, such as the smalt in the Trippenhuis samples and in the Steen. The smalt particles also appear more transparent in a transparent brown matrix where all the lead white has transformed into soaps than when embedded in reflecting lead white particles. This also has to do with differences in RI, the difference between lead white and smalt (RI: 1.47-1.55) is much larger than that between smalt and lead soaps or the oil medium.

These sorts of alterations involving the increased transparency of ground and paint layers as a result of saponification processes may have a larger impact on the

---

20 In the Aert van der Neer painting, a color change may also take place due to interaction of the lead soaps with the partially dissolved umber particles. Partial dissolution of umber facilitated by the basic conditions is also held responsible for the differences in tone in the umber particles that range from red to brown. The De Mayerne manuscript warns that umber-containing paints can darken and become dull. Mention is made of a process known as bleeding [Van Eikema Hommes 1998, pp. 114-115, 129]. According to Hess [Hess 1979] “bleeding” refers to the diffusion of a coloring matter [...] and also to the discoloration resulting from such diffusion.
changing appearances of oil paintings than is often considered. However, to what extent this has occurred is difficult to assess, and is perceptible usually only in the most extreme cases. We hope that the results presented in this paper will be a starting point for more systematic and quantitative studies. In the next sub-section, we will further discuss the phenomenon of the localized darkening on the wood grain.

**LOCALIZED DARKENING ASSOCIATED WITH THE WOOD GRAIN**

The analyses have shown that differences in the thickness of the ground in relation to the panel’s wood structure correspond with different degrees of lead soap formation in the layer. We propose that the fatty acids required for the soap formation are partly supplied by the thick areas of chalk ground that selectively fills the early wood channels.\(^{21}\) This explains the relationship between the thickness of the ground and the degree of lead soap formation. Moreover, a large amount of oil (mostly as free fatty acids), required for the transformation of lead white into lead soaps, was detected with DTMS in the chalk ground from all four paintings.

Since there is no evidence in the documentary sources to suggest oil was added expressly to chalk grounds at this time\(^{22}\), we therefore have to conclude that the oil (and resin) components identified in the chalk/glue ground was most likely absorbed from the oil paint (and varnish) layers above. This was borne out of recent DTMS analyses of ground reconstructions comprising animal glue-bound chalk grounds covered with different types of oil-based imprimaturas. Here DTMS confirmed the absorption of oil components in the chalk grounds.\(^{23}\) The presence of oil in the chalk/glue ground also explains its lack of reflectivity and role in the localized darkening. Light can penetrate even deeper allowing the ground, and possibly also the panel, to shine through the transparent upper layer(s). In the four case studies presented here, the chalk ground has been deliberately applied very thinly, only filling the wood grain. In the darkened areas in the Van Goyen (*River View*) and Jan Steen, the lead white-containing *imprimatura* in the painting is also very thin, and seems to have been partly absorbed by the chalk ground thus explaining the loss of light reflectivity of the grounds in these paintings. Of course, it is difficult to know how reflective/absorbent the chalk grounds originally were, and indeed some chalk grounds appear more transparent and browner than others. In this sense, the thickness/porosity of the grounds is considered to be a decisive factor in the final appearance of paintings.

As to what may have triggered the saponification process resulting in selective darkening, fluctuations in temperature and relative humidity are considered to play an important role. Since the porous early wood with the thickest areas of chalk ground is expected to absorb more moisture, as compared to the denser latewood, the influence of moisture will be greater for the paint on top of the early wood. Furthermore, a chalk ground is hygroscopic and is likely to respond to humidity changes. Swelling

---

\(^{21}\) Acidic emissions or extracts from the wood do not seem to play a significant role in the darkening process as initially thought, since the thick chalk ground in the darkened areas would act as a buffer to neutralize acidic compounds.

\(^{22}\) Personal communication Maartje Witlox 2007.

\(^{23}\) Ground reconstructions were provided by Maartje Witlox and Tiarna Doherty 2007.
Fig. 5.13 Schematic diagram showing the gradual dissolution and saponification of lead white in the upper paint layer and explaining the effect of saponification on the reflectance of light and on the surface appearance. Stages 1-5: (1) intact paint, light is scattered (2) early stage, first the small lead white particles react away, (3) mature stage, the small particles have reacted away, edges of the large particles are also dissolving, (4) late stage, the large particles are almost dissolved, (5) final stage, all lead white is saponified, light is absorbed.
and shrinking of the thick chalk ground may have played a role in causing the surface paint to flake off in these areas exposing the darkened *imprimatura*. However, as already pointed out, a saponified lead white layer takes up a larger volume than it originally had;\(^{24}\), in this sense the physical expansion of the affected layer explains the paint loss associated with the early wood.\(^{25}\)

The fact that this particular phenomenon is often observed in early to mid-seventeenth-century panel paintings has to do with a number of factors: not only the use of coarsely grained oak panels,\(^{26}\) but also a change in painting technique involving the use of thin ground and paint layers. The stylistic changes that had come about as a result of this faster and more economical approach resulted in open brush work, the use of thin and often translucent oil-rich paint layers, and a simple paint layer build up, consisting of one or at most two paint layers. In this sense, this type of degradation is technique dependent.

Alterations, such as darkened lines, changes in tone and contrast, and the associated color change and loss of detail, naturally can have profound consequences for the interpretation of the pictorial, illusionistic and aesthetic intentions of the artist. However, with some artists, caution has to be exercised because the use of transparent ground layers may be part of the artist’s technique that allowed the color and structure of the panel to play a role. This is the case with Jan van Goyen, particularly in his mature works where even the lines of the wood grain are sometimes incorporated as a pictorial element, for instance as ripples in the water [Gifford 1996: 74-77]. However, one has to be careful not to misinterpret lines, such as we see in River View, as deliberate effects. Here, the surface paint is thin or has flaked off exposing the darkened *imprimatura* and thus taking on an unintended pictorial role. Moreover, in the thinly painted sky the horizontal lines produced by exposure of the darkened *imprimatura* due to flaking and cracking of the surface paint have formed an additional pattern that was never intended by the artist.

To achieve his artistic goals Van Goyen applied an extremely thin chalk/glue ground, just filling the wood grain. The use of such thin grounds that scarcely fills the wood grain seems to represent a change in painting technique, since most recipes for chalk/glue grounds from the fifteenth to the seventeenth centuries state that the ground should be applied in several layers. In 1604, Van Mander mentions that earlier artists

\(^{24}\) Conversion of lead white into lead soaps, calculated on a molar basis, leads to a 26x increase in volume compared to the original volume of 1M of lead white, assuming that the fatty acids come from elsewhere and do not leave a negative volume (Frank Hoogland, FOM-AMOLF 2007). Therefore, the volume change can be considerable in a complex lead white paint layer where fatty acids possibly migrate from the pore space of another layer. Volume increase by a factor of two or three would already have a large effect on the physical strength of such a paint layer complex.

\(^{25}\) Shrinkage across the grain may also play a role in the delamination of the paint, since both the underlying wood and chalk ground are hygroscopic and undergo tangential expansion and compression. Two early panel paintings from 1480/90 and 1546, one on red beech with a chalk ground and the other on oak with a red lead ground, demonstrate similar localized damage and paint loss [Bünsche 1993].

\(^{26}\) By nature, oak is a ring-porous wood, its coarse structure easily recognized because of the formation of bands of large early wood vessels to conduct water, followed by the formation of more compact late wood with smaller vessels [Klein 1998: 39, 40].
used to ground their panels more thickly [Miedema 1973], while Willem Beurs in 1692, says that the chalk ground only needs to fill the pores of the wood [Beurs 1692]:

…Our modern ancestors before used to whiten their panels more thickly / and scraped them as smooth as they could / also used cartons / which they applied to this even beautiful white / and sat down to trace them with some material that rubbed off / applied to the back / then they drew on neatly with black chalks or pencils…

[translation by M. Witlox].

[Van Mander 1604: 256, 257, fol. 47v]

…One first lays on the panel a ground of weak glue mixed with white chalk to cover the grain of the wood; after this one must scrape it off and make the panel smooth and even, taking care that the grain remains filled. After this one grinds umber and lead white very thickly with oil and applies it to the panel first with a knife, after which one smooths it with the hand; [do this] 3 to 4 times depending on how smooth one wants it to be, and thus is it ready for a painter of images, but for a landscape painter, one takes black mixed with lead white…

[translation by P. Noble and M. Witlox].

[Beurs 1692: 19-20]

Because of its great impact on the tonality and the long-term effects on the appearance of paintings, the nature of the ground attracts considerable attention in historical sources. In 1839 Henri Fielding refers to Van Goyen’s (and others) use of transparent grounds as being ‘the destruction of many fine pictures’ stating that ‘…Van Goyen and others have prepared or filled up the pores of the wood with their transparent vehicle, which also enabled them to shew [original spelling] the grain of the wood through the shades of the subject’. [Fielding 1839: 81-82]. Even though Van Goyen made deliberate use of transparent grounds, it would appear that two centuries later, Fielding is referring to an increase in
the transparency of Van Goyen’s paintings due to the loss of hiding power in the priming and paint layers as has been described in this paper.  

**CONCLUSION**

Due to the insights gained about metal soap formation, the conversion of particulate mineral lead white and lead-tin yellow to organic complexes of metal soaps is considered to play a major role in increasing transparency, and the consequent darkening of oil paints containing lead white or lead-tin yellow pigment. SEM backscatter images of paint cross-sections from affected paintings reveal the gradual transformation of highly scattering well-defined pigment particles into less dense (grayer) amorphous lead soap areas. This chemical change, which results in the decreased ability of lead white and lead-tin yellow to scatter light, explains the reduction in hiding power. The visual impact of this phenomenon on the appearance of paintings can be significant, as seen in the seven paintings presented in this study. Not only the degree of saponification, but also the other coloring components in the affected paints and the presence of a dark(ened) underlayer are decisive factors in the final appearance of the paint at the surface.

Loss of opacity has also been found to occur selectively. The investigations of the panel paintings by Aert van der Neer, Jan van Goyen and Jan Steen revealed that the paint on top of the porous early wood on the radial surface appeared darker in relation to the nearby intact paint on the late wood. These darkened areas were found to be associated to localized lead soap formation in the lead white-containing priming/paint layers as a function of the thickness of the chalk grounds that fills the uneven structure of the wood grain. As a consequence, the darkened *imprimatura* either shimmered through the thin translucent sky paint or was exposed as a result of loss of the sky layer due to swelling of the underlying saponified priming layer creating disturbingly dark stippled lines.

It is part of the restorer’s job to bring back the balance in the picture and improve the readability. However, the question remains how far one wants to go with retouching, especially when the darkening involves large areas of the painting. In the Aert van der Neer, careful retouching was necessary to hide the lines in order that the picture could be displayed in the galleries; after retouching the painting is closer to its original appearance. This will also be the case with the Jan Steen painting. As for the Van Goyens, they are no longer displayed in the galleries. Given Van Goyen’s predilection for transparent paint layers, the striped pattern of lines covers most of the surface and despite the fact that the aesthetic, pictorial and illusionistic intentions of the artist are compromised, it remains questionable as to whether one should consider retouching or overpainting such a large area. Likewise, in the Savery and the Trippenhuis ceilings, the darkening involves large areas of the painting. Some restorers employ selective cleaning as a solution, or apply thin tinted glazes on light or bright areas in the painting that

---

27 Maartje Witlox is thanked for pointing out the relevant historical sources from the HART database.
contrast too strongly with the darkened areas in order to repair/restore the unity in a picture.

ACKNOWLEDGEMENTS

The close collaboration with the Conservation studio of the Mauritshuis, particularly with Petria Noble and Sabrina Meloni, as well as the architectural paint researchers of the Trippenhuis ceilings, Edwin Verweij and Ruth Jongsma, is gratefully acknowledged. Thanks are also extended to Maartje Witlox for sharing data from the HART ground recipe-database (De Mayerne Research Program 2004-2006), as well as Jerre van der Horst, FOM Institute AMOLF, for his kind assistance with the DTMS analyses.

REFERENCES

Beurs, W., 1692, *De groote Waereld in het Kleen Geschildert*, Johannes en Gillis Ansonius van Waesberge, Amsterdam.


Summary

The oil paints used by the seventeenth-century painters as discussed in this thesis are extremely complex and dynamic systems. Paintings are, in fact, subject to all kinds of chemical and physical processes taking place on a micro and molecular level in the paint layers that over time become visible changing the original appearance of the work of art. The main subject of this thesis is degradation phenomena as encountered in seventeenth-century oil paintings by Dutch Masters, among which are color changes, crust formation, increased transparency and darkening. It includes a large number of case studies from museum collections and historic interiors, in particular the Royal Picture Gallery Mauritshuis and the Oranjezaal ensemble in the Royal Palace Huis ten Bosch. The paint compositions and the chemical and physical processes responsible for the degraded appearances of the paintings were investigated in minuscule paint samples using various microscopic and analytical techniques. The acquired information on alteration processes is not only of direct relevance for the art historical interpretation but also for the treatment and re-presentation of the work of art.

Chapter 1 addresses the preparation of paint cross-sections and the various microscopic and analytical techniques used for painting studies, mostly developed during the MOLART and De Mayerne programs. It illustrates the importance of high-quality surface preparation for analytical imaging studies of paint cross-sections. A systematic dry polishing method was developed, based on mechanical preparation with the sample fixed in a polishing holder. Using this method, the surface of existing paint cross-sections was re-polished and re-measured resulting in higher quality analytical data. A cross-section from the flesh paint of a polychrome sculpture by Franz Ignaz Günther - Saint Isidor, c.1765, Abbey Church in Rott am Inn - was studied using specular reflection Fourier transform infrared (SR-FTIR) imaging. This sample shows a complicated layer structure with a thin, medium-rich intermediate layer that after improvement of the surface could be interpreted as a proteinaceous isolation layer. In the second example, we analyzed the thick, yellowed varnish on a painting by Vincent van Gogh, Falling Leaves (Les Alyscamps), 1888, Kröller Müller Museum, inv. no. 224. SR-FTIR imaging of the cross-section revealed, after re-polishing, that the thick varnish layer in fact consisted of two separate layers with different compositions, a resinous layer and a proteinaceous/carbohydrate layer. In the last example, a cross-section from a painting by Johannes Vermeer - Diana and her Companions, c.1655, Mauritshuis, inv. no. 406 - was examined using static-Secondary Ion Mass Spectrometry (SIMS). This analysis was performed within the context of the research on lead carboxylate aggregate formation in lead-tin yellow paints. Here, the higher surface quality led to better mass and spatial resolution.

Chapter 2 describes natural ageing processes in the seventeenth-century oil paintings of the Oranjezaal ensemble in the Royal Palace Huis ten Bosch (The Hague). Degradation of a wide range of pigments – lead white, lead-tin yellow, red lead, smalt, azurite, blue
verditer, verdigris, ultramarine, vivianite, orpiment, vermilion, bone black, *schiet*-yellow, red lake, indigo and Kassel earth – in oil paints was investigated. In the case of this unique ensemble, remained in situ under known conditions with minimal intervention since 1650, it was possible to relate the degree of ageing to differences in quality of pigment and binding medium and the ways in which the artists applied their materials. It was essentially the initial choices of materials by the artist himself that accounted for the observed differences in degradation.

Material analyses demonstrated that most painting materials were not homogeneous and that the differences in quality depending on the source and manufacture were found to affect the stability. Due to pigment-medium interaction resulting in leaching of the potassium from the potash glass, the blue smalt oil paints now have a grayish or brownish color. The smalts varied in particle size, which influences the rate of discoloration, the small particles loosing their color first.

Also, the paints containing the blue vivianite now have a grayish or brownish appearance, probably as a result of oxidation of iron (from (II) to (III)). The vivianite, most likely collected from local deposits in the Netherlands associated with peat bogs, has a particular fine particle distribution. Possibly in combination with the fact that it was used in oil, these fine particles made the pigment more susceptible to oxidation.

Whitish spots and streaks were observed in many of the dark paints containing bone black. Cross-sectional analyses demonstrated that part of the bone black particles have lost their color and now appear whitish. We proposed that the carbonized organic matter in bone black responsible for the black color has reacted away in the presence of lead (and manganese). The composition and stability of bone black were found to depend on the manufacture, specifically the heating conditions of the animal bones (temperature and time of exposure). Incomplete carbonization resulted in poor quality bone black or bone brown.

The lead-tin yellow type I paints were affected by the formation of lead soap aggregates, the whitish translucent masses causing a gritty surface texture. Apart from lead-tin oxide (lead ortho-stannate), tin oxide clusters and (residual) lead oxide were detected in the original lead-tin yellow pigment demonstrating the inhomogeneous composition of the pigment probably due to varying reaction conditions in the production process. Lead oxide is particularly reactive to fatty acid compounds from the oil medium and reacts to lead soaps. The expensive red vermilion was sometimes found to be adulterated with red lead, reducing the stability of the paint. Red lead is also very reactive towards the oil medium and easily forms lead soap aggregates. The soap masses formed in an underlying vermilion/red lead-containing layer protrude through the paint surface covering it with crater-like holes filled with whitish (mineralized) soap material.

It seems that blue verditer mixed with yellow lakes and other pigments replaced the green glazes based on verdigris that have the strong tendency to become opaque brown over time. The light-sensitive red organic lake glazes were generally well-preserved. They were found to consist mostly of the high-quality alum-substrated cochineal. In a few strongly degraded glaze layers, substantial amounts of calcium carbonate and calcium sulfate were detected, possibly residual substrates of a now
faded organic lake pigment. Dyestuffs precipitated on chalk are considered less stable compared to those on alumina substrates. The use of a chalk substrate is mentioned in contemporary recipes to be used with the less valuable and less stable organic lakes, the yellow lakes/schiet yellows and those derived from brazilwood.

In addition, it could also be shown that the pigment combination and layer structure influence the reactivity of the paint. For example, the degraded appearance of the blue draperies painted with the precious ultramarine appeared to be mainly the result of the use of cheaper and less permanent colors, smalt and vivianite, in the underpainting, smalt and vivianite. The application of red organic glazes over a red vermilion underpainting prevented the light-sensitive vermilion from blackening and graying, making the red color more permanent. Additionally, the admixture of lead white to vermilion, ultramarine and smalt paints seems to have made these paints less susceptible to discoloration, probably owing to the strong coordinating properties of lead white with the oil network. With the light-sensitive organic pigments, such as the yellow and red lakes, organic browns (Kassel earth) and blue indigo, however, the presence of lead white significantly accelerates the fading process, due to the lower pigment concentration and the light-reflective properties of the white pigment. Furthermore, the application of a thick multi-layered system has prevented blue surface layers with indigo from color loss. The yellow highlights applied with orpiment are now sunken in with raised edges. This may be due to improper use of the pigment, for instance the utilization of a slow drying oil or application over an underlying paint that had not dried completely.

It was demonstrated that, even under these mild environmental conditions, the paints are subject to all kinds of chemical processes that have changed the original appearance of the paintings. However, most of the paintings are still in excellent physical condition owing to the high-quality preparation of the canvases, and to minimal intervention. According to a contract that has survived, the canvas supports were prepared with a uniform, light beige-colored ground by the primer François Oliviers. The grounds were shown to generally consist of lean lead white paint, ground in linseed oil, with small additions of brown umber.

It was concluded that the artist’s choice of materials was not only dictated by their durability, but as much by their availability, price and the painterly/optical effects he wanted to achieve.

The following three chapters include more in-depth studies of specific degradation phenomena that have a strong impact on the changing appearances of oil paintings, i.e., the whitening of the bone black pigment (Chapter 3), the more widespread phenomenon of white hazes and crusts on dark oil paint films (Chapter 4), and the increased transparency of the lead-containing oil paint (Chapter 5). It is demonstrated that the formation and mobility of metal (lead) soaps also play a prominent role in these paint defects.
The whitening of black paints in the paintings of the Oranjezaal could not easily be accounted for and required further examination. Degradation of black paints in the Oranjezaal was essentially associated with the use of bone black, a black pigment made from charred bones of animals. Chapter 3 describes the whitening phenomenon of the bone black pigment that changed color from black into white. This phenomenon has not been reported before in oil paintings. Whitish spots and streaks were observed in the dark paint of no fewer than seven paintings by Pieter Soutman, Gerard van Honthorst, Gonzales Coques, Jacob van Campen, and Jacob Jordaens (an area painted by Van Honthorst). As a result, areas originally intended as black and dark brown – hair, eyes, shadows – have dramatically changed in appearance. Analytically, bone black can be easily distinguished from other carbon black by its high percentage of hydroxyapatite, a calcium phosphate phase and the principal mineral component in bone (70-80 per cent by mass), in addition to carbon (10-20 per cent by mass). Cross-section analyses reveal that part of the bone black particles have lost their color and now appear whitish. The white particles strongly fluoresce in UV light, whereas intact bone black appears dark. Another significant feature, evident from the EDX analyses, is the adsorption of lead and manganese (as salts or soaps?) by the porous bone black particles. The lead and manganese are thought to originate from pigment particles present in the black layer(s) or the underlying lead white-containing ground. In contrast, EDX maps and FTIR images revealed homogeneous distributions of phosphate, phosphorus and calcium over the intact and whitened bone black. Therefore, a conversion of the calcium phosphate substrate as accounted for the color change was thus not observed. It is proposed that the carbonized organic matter in bone black responsible for the black color had reacted away in the presence of lead. The conditions under which the bone black was made must have influenced the stability of the pigment. The X-ray diffraction pattern of the bone black samples reveal an amorphous or poorly crystalline hydroxyapatite indicating that the bone black was prepared at relatively low temperature. This suggested a poor quality bone black or the intentional use of bone brown, formed by incomplete carbonization.

The whitening of the dark paints in paintings by Pieter de Grebber and Salomon de Bray was caused by the formation of insoluble white hazes and crusts on the paint surface, which is the topic of Chapter 4. This chapter also presents examples from other museum collections, The Royal Picture Gallery Mauritshuis and the Staatliche Museen Kassel, and from historic interiors, such as the Johan de Witt House in The Hague and the Trippenhuis in Amsterdam. In total ten case studies are discussed in detail. They varied in display and restoration history. The whitening was mainly confined to the dark areas in the pictures, suggesting a strong influence of the composition of these dark medium-rich paints. They were found to contain bone black or carbon black mixed with earth pigments, smalt and red and yellow lakes. The chemical processes that take place in these paint layers are shown to be largely comparable.

In some cases, the whitish surface layers were found to 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 are an original part of the
paint build-up. Frequently, calcium oxalates and lead chlorides were associated with the degradation of these calcareous layers. The whitened shadow areas in the background of the Portrait of a Standing Man by Rembrandt (1639, Staatliche Museen Kassel, inv. no. 239), the affected dark boots in the Triumphal Procession with Spoils of War by Pieter de Grebber (1648, Oranjezaal, No. 24), the grayed surface of the dark cloak of the old man in Salomon de Bray’s Triumphal Procession with Musicians (1649, Oranjezaal, No. 26) and the wood grain-related whitening in the dark interior of the Departure from the Stable by Philips Wouwerman (1655-65, Mauritshuis, inv. no. 215) belong to this group.

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 interacted with the atmosphere to form new stable mineral phases (carboxylates, sulfates, oxalates, carbonates). The whitish surface deposits in the painted ceilings of the Johan de Witt House (The Hague, 1652-55) and the Oranjezaal by Pieter de Grebber, The Ascension of Frederik Hendrik into Heaven (1650, No. 22), were found to largely consist of lead soaps and mineralized lead soaps (lead sulfate), while analyses of the surface deposits in Rembrandt’s Homer (1663, Mauritshuis, inv. no. 584) and Simeon’s Song of Praise (1631, Mauritshuis, inv. no. 145), Frans Hals’ Portrait of Jacob Olycan (1625, Mauritshuis, inv. no. 459) and the Trippenhuis ceilings painted with hunting scenes with skies and birds (Amsterdam, 1660-62) show more complex crust compositions. In these latter paints, potassium and calcium in addition to lead were involved in the crust formation. The lead soaps resulted from dissolution of lead white present in an underlying layer. Potassium was associated with various pigment sources, primarily smalt, but also earth pigments and/or substrates of lake pigments. This shed new light on the reactivity of these dark paints. The mobilization processes were likely to be 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 heat from a fire. It was proposed by Robert Corkery that the metal soaps were able to move as monolayers on water films or were readily diffusable 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. It seems that these medium-rich porous dark paints were particularly susceptible to the formation and subsequent transport of metal soaps to the surface. Environmental conditions and possibly past treatment were 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. At the end of this chapter, the consequences of metal soap mobility for the interpretation of analytical data were also discussed, as well as the implications for conservation.

The darkening of oil paint films as a result of increased transparency is the subject of Chapter 5. This disturbing phenomenon was observed and noted for a long time in paintings. Due to the insights gained about metal soap formation, the conversion
of particulate mineral lead white and lead-tin yellow to organic complexes of metal soaps is considered to play a major role in increasing transparency, and the consequent darkening of oil paints containing lead white or lead-tin yellow pigment. Case studies from the Royal Picture Gallery Mauritshuis and the Tripenhuis are presented. SEM backscatter images of paint cross-sections from the affected paintings reveal the gradual transformation of highly scattering well-defined pigment particles into less dense (grayer) amorphous lead soap areas. This chemical change, which resulted in the decreased ability of lead white and lead-tin yellow to scatter light, explains the reduction in hiding power. The visual impact of this phenomenon on the appearance of paintings could be significant, as seen in the seven paintings presented in this study. Not only the degree of saponification, but also the other coloring components in the affected paints and the presence of a dark(ened) underlayer are decisive factors in the final appearance of the paint at the surface. As with the yellow stockings in the Draughts Players by Michael Sweerts (1652, Mauritshuis, inv. no. 1121), the darkening effect observed on the surface is enhanced by the dark, almost black underlayer that shimmers through the yellow layer containing lead-tin yellow that has become increasingly transparent. The loss of the white pigment in medium to dark paint layers as a result of saponification may also lead to color changes that can have a great visual impact on paintings, the dark areas of the painting becoming thus much darker than originally intended. This was seen for example in Orpheus enchanting the Animals with his Music by Roelandt Savery (1627, Mauritshuis, inv. no. 157), where darkening of the brown and gray medium tones in the foreground had resulted in a noticeable distortion of the original light/dark contrasts: the animals disappeared in the foreground, and the dark foreground stands out too strongly against the light, blue sky. Particularly interesting was also the effect of increased transparency of the surrounding medium on the hiding power and color intensity of other pigments in the layer, such as the smalt. This was noticed in the discolored sky paints from the Tripenhuis ceilings painted with hunting scenes with skies and birds (Amsterdam, 1660-62). The smalt particles appear more transparent and discolored in a transparent brown matrix where all the lead white has transformed into soaps than when embedded in reflecting lead white particles. The blue light reflected by the smalt is mostly absorbed by the brownish matrix.

Loss of opacity has also been found to occur selectively. The investigations of the panel paintings by Aert van der Neer, River Landscape (mid-1650s, Mauritshuis, inv. no. 912), Jan van Goyen, Dilapidated Farmhouse with Peasants (1631, Mauritshuis, inv. no. 1081) and River View (c.1644-48, Mauritshuis, inv. no. 759), and Jan Steen, Dancing Peasants at an Inn (c.1644-48, Mauritshuis, inv. no. 553), reveal that the paint on top of the porous early wood on the radial surface appears darker in relation to the nearby intact paint on the late wood. These darkened areas were found to be associated to localized lead soap formation in the lead white-containing priming/paint layers as a function of the thickness of the chalk grounds that fills the uneven structure of the wood grain. As a consequence, the darkened imprimatura either shimmers through the thin translucent sky paint or was exposed as a result of loss of the sky layer due to expansion of the underlying saponified priming layer creating disturbingly dark stippled lines.
Summary

The loss of reflectivity of the chalk ground by absorption of oil from the paint layers (as demonstrated by the DTMS data) also contributed to the darkening effect since light could penetrate deeper into the painting. The presence of oil in the chalk ground also explains the source of free fatty acids required for the transformation of lead white into lead soaps. That this is often observed in panel paintings around the middle of the seventeenth century is technique-related: there is not only a preference for the use of coarse-grained oak panels and lead white-rich *imprimatura layers*, but also for thin absorbent chalk grounds, simple paint build-up and open brush work.

These kinds of alterations involving the increased transparency and consequent darkening of the oil paint as a result of metal soap formation may have a larger impact on the changing appearances of oil paintings than is often considered. However, it remains an open question how to re-present the work of art, especially when the darkening involves large areas of the painting. How far can one go with retouching such large areas?
Samenvatting


In Hoofdstuk 1 komen de preparatiemethoden van verfdwarsdoorsneden en diverse microscopische en analytisch-chemische onderzoekstechnieken aan de orde die bij schilderijenstudies worden toegepast, waarvan de meeste zijn ontwikkeld gedurende de MOLART en De Mayerne programma’s. Het illustreert het belang van een hoge kwaliteit oppervlakte bewerking voor analytisch-chemische imaging studies van verfdwarsdoorsneden. Een systematische droge-polijst-techniek werd ontwikkeld, gebaseerd op mechanische preparatie met het verfmonster gefixeerd in een polijsthouder. Met behulp van deze polijsttechniek werd het oppervlak van reeds geprepareerde verfdwarsdoorsneden opnieuw gepolijst en vervolgens met behulp van Fourier transformatie infra-rood (SR-FTIR) imaging. Dit monster vertoonde een gecompliceerde laagstructuur, waaronder een dunne, bindmiddelrijke tussenlaag die na verbetering van het oppervlak kon worden geïnterpreteerd als een eiwithoudende isolatielaag. Het tweede voorbeeld is de dikke, vergeelde vernis op een schilderij van Vincent van Gogh, Vallende bladeren (Les Alyscamps), 1888, Kröller Müller Museum, inv. no. 224. SR-FTIR imaging van de verfdwarsdoorsnede onthulde, na herpolijsten, dat de dikke vernislaag in feite bestond uit twee aparte lagen van verschillende samenstelling die in beeld konden worden gebracht: een natuurlijke harshoudende laag op een uiwit-/koolhydraathoudende laag. Als laatste voorbeeld werd een dwarsdoorsnede uit een schilderij van Johannes Vermeer – Diana en haar nimfen, c.1655, Mauritshuis, inv. no. 406 – onderzocht met behulp van
statische-Secondaire Ionen Massaspectrometrie (SIMS). Deze analyse werd uitgevoerd als onderdeel van het onderzoek naar de vorming van loodcarboxylaat-aggregaten in loodtingeelverf. In dit geval leidde een hogere oppervlakte kwaliteit tot een betere massa-en plaatsresolutie.

**Hoofdstuk 2** beschrijft natuurlijke verouderingsprocessen in de zeventiende-eeuwse olieverfschilderijen van het Oranjezaal ensemble in het Koninklijk Paleis Huis ten Bosch (Den Haag). De degradatie van een groot aantal pigmenten – loodwit, loodtingeel, vermiljoen, beenderzwart, schietgeel, rode lak, indigo en Kasselse aarde – in olieverven worden behandeld. In het geval van dit unieke ensemble, dat sinds 1650 altijd onder bekende omstandigheden in de zaal verbleef en met minimale interventie was onderhouden, bleek het mogelijk om de mate van veroudering te relateren aan verschillen in kwaliteit van pigment en bindmiddel en de wijze waarop de kunstenaar de materialen verwerkte en toepaste. Het was met name de keuze van de kunstenaar zelf voor bepaalde materialen die de geobserveerde verschillen in degradatie verklaarden.

Materiaalanalyses hebben bewezen dat de meeste schildersmaterialen niet homogeen zijn en dat de verschillen in kwaliteit, afhankelijk van de bron en productie, de stabiliteit beïnvloeden. De blauwe smalthoudende olieverven hebben nu een grijzige of bruinige kleur, als gevolg van een pigment-medium interacties die resulteerden in het uitlopen van kalium uit het glas. De smalten varieerden in deeltjesgrootte, hetgeen de snelheid van het ontkleuringproces beïnvloedde. De kleine smaldeeltjes ontkleurden het eerst.

Ook de verven met het blauwe vivianiet hebben nu een grijzige of bruinige uiterlijk, waarschijnlijk door oxidatie van het element ijzer (van (II) naar (III)). Vivianiet werd zeer waarschijnlijk gedolven uit locale afzettingen in veenmoerassen die in de zeventiende eeuw in Nederland veel voorkwamen. Het lijkt er op dat deze Hollandse vivianiet een bijzonder fijne deeltjesverdeling heeft zoals naar voren kwam uit bestudering van de verfdwarsdoorsneden. Mogelijk in combinatie met het feit dat het in olie was gebruikt, maakten de fijne deeltjes het pigment meer gevoelig voor oxidatie.

Witte vlekken en strepen zijn aangetroffen in veel van de donkere verven die beenderzwart bevatten. Dwarsdoorsnede analyses lieten zien dat een deel van de beenderzwart deeltjes hun kleur hadden verloren en er nu wittig uitzien. Aangenomen werd dat het verkoolde organische materiaal in beenderzwart, dat verantwoordelijk is voor de zwarte kleur, is weggereageerd door de aanwezigheid van lood (en mangaan). De samenstelling en stabiliteit van beenderzwart bleek ook afhankelijk van het productieproces, in het bijzonder de verhittingsomstandigheden van de dierlijke botten (temperatuur en blootstellingstijd). Onvolledige verkering/carbonisatie resulteert in een slechte kwaliteit beenderzwart of wellicht in beenderbruin.

De loodtingeel type I verven zijn aangetast door de vorming van loodzeepaggregaten, waarbij de wittig doorschijnende bolletjes een korrelige oppervlaktestructuur veroorzaken. Behalve loodtinoxide worden ook tinoxide clusters en lood(II)oxide gevonden in het oorspronkelijke loodtingeel pigment. Dit duidt op een inhomogene samenstelling van het pigment door variabele reactieomstandigheden
Color changes and chemical reactivity in seventeenth-century oil paintings

in het productieproces. Lood(II)oxide reageert sterk met vetzuurcomponenten uit het oliebindmiddel tot loodzepen.

Het dure rode vermiljoen werd soms versneden met loodmenie, hetgeen de stabiliteit van de verf niet ten goede kwam. Loodmenie reageert ook sterk met het oliebindmiddel en vormt gemakkelijk loodzeepaggregaten. De zeepmassa’s die in een onderliggende vermiljoen-/meniehoudende laag werden gevormd zijn door het verfoppervlak heengebroken en bedekken het oppervlak nu met kraterachtige gaatjes, die gevuld zijn met een wittig, deels gemineraliseerd metaalzeepmateriaal.

Het blijkt dat blauw verditer gemengd met schietgeel en andere pigmenten werd gebruikt in plaats van een groene glacis op verdigris basis dat lange tijd veelvuldig was gebruikt als groen pigment maar dat sterk de neiging heeft om na verloop van tijd opaak bruin te worden. De lichtgevoelige organische rode lak glazeringen zijn in het algemeen goed bewaard gebleven. Ze bestaan meestal uit hoge kwaliteit cochenille neergeslagen op aluminiumsubstraat. In een paar sterk gedegradeerde glacislagen werden aanzienlijke hoeveelheden calciumcarbonaat en calciumsulfaat aangetroffen, mogelijk achtergebleven substraten van een nu verbleekt organisch lakpigment. Een kalksubstraat werd volgens de eigentijdse recepten gebruikt in combinatie met de minder kostbare en minder stabiele kleurstoffen, zoals als gele of die bereid waren uit brazielhout.

Het blijkt dat ook de pigmentcombinatie en laagstructuur van invloed zijn op de reactiviteit van de verf. Het gedegradeerde uiterlijk van de blauwe draperieën bijvoorbeeld, geschilderd met het kostbare ultramarijn, blijkt met name te wijten aan het gebruik van goedkopere en minder permanente kleuren, smalt en vivianiet, in de onderschildering. Het aanbrengen van een rode organische glacis over een rode vermiljoen houdende onderschildering beschermt het lichtgevoelige vermiljoen tegen zwart of grijs worden en maakt derhalve de rode kleur bestendiger. Ook blijkt de toevoeging van loodwit aan vermiljoen-, ultramarijn-, en smaltverf deze vrenen minder gevoelig te maken voor verkleuring, waarschijnlijk door de sterke coördinerende eigenschappen van loodwit met het olienetwerk. Bij de lichtgevoelige organische pigmenten, daarentegen, zoals de gele en rode lakken, de organisch bruinen (w.o. Kasselse aarde) en het blauwe indigo, versnelt eenzelfde toevoeging het verblekingsproces aanzienlijk als gevolg van de lagere pigmentconcentratie en de lichtreflecterende eigenschappen van het witte pigment. Voorts verhindert het aanbrengen van een dik verfsysteem, opgebouwd uit meerdere lagen, kleurverlies van de blauwe partijen die zijn uitgevoerd met indigo. De gele hooglichten van orpimentverf waren nu in het midden ingezakt en hebben opstaande randen. Waarschijnlijk is het pigment op onjuiste wijze verwerkt, bijvoorbeeld met een langzaam drogende olie en was het aangebracht op een onderliggende verf die nog niet helemaal was gedroogd.

Het is nu aangetoond dat zelfs onder de milde omgevingscondities in de Oranjezaal de vrenen onderhevig zijn aan allerlei chemische processen, die de oorspronkelijke verschijning van de schilderijen hebben veranderd. De meeste schilderijen zijn echter nog steeds in uitstekende fysische conditie dankzij de hoge kwaliteit van de dragers en preparatielagen, en de minimale ingrepen. Volgens een overgeleverd contract zijn de doeken geprepareerd met een uniforme, lichte beige
Samenvatting
gekleurde grond door de primuurder François Oliviers. Uit analyses is gebleken dat de grondlagen in het algemeen bestaan uit een magere loodwitverf, gewreven in lijnzaadolie, met kleine toevoegingen van bruine omer.

Onze conclusie is dat de materiaalkiezen van de kunstenaar niet alleen werden bepaald door hun duurzaamheid, maar evenzeer door hun beschikbaarheid, prijs en de schilderkunstige effecten die de kunstenaars wilden bereiken.

De volgende drie hoofdstukken bevatten meer diepgaande studies van specifieke degradatieverschijnselen die een sterke uitwerking hebben op de veranderende verschijning van olieverschilderijen, zoals het witworden van het beenderzwart pigment (Hoofdstuk 3), witte was- en korstvorming op donkere olieverffilms (Hoofdstuk 4) en de toenemende transparantie van loodhoudende olieverven (Hoofdstuk 5). Het is duidelijk dat de vorming en mobiliteit van metaal(lood)zepen ook een prominente rol spelen bij het ontstaan van deze verfdefecten.

Het witworden van zwarte verf in de schilderijen van de Oranjezaal is niet makkelijk te verklaren en vereiste nader onderzoek. Degradatie van zwarte verf was voornamelijk geassocieerd met het gebruik van beenderzwart, een zwart pigment gemaakt van verkoelde botten van dieren. **Hoofdstuk 3** beschrijft het witworden van het beenderzwart pigment dat van kleur verandert van zwart naar wit. Dit verschijnsel is niet eerder beschreven voor olieverfschilderijen. Witte vlekken en strepen zijn te zien in de donkere verf van maar liefst zeven schilderijen van de hand van Pieter Soutman, Gerard van Honthorst, Gonzales Coques, Jacob van Campen, en Jacob Jordens (het onderdeel geschilderd door Van Honthorst). Als gevolg hiervan is het uiterlijk van oorspronkelijk zwart en donkerbruin bedoelde delen – haren, ogen, schaduwpartijen – dramatisch veranderd. Analytisch kan beenderzwart makkelijk worden onderscheiden van ander koolstofhoudend zwart aan de hand van zijn hoge aandeel hydroxyapatiet (calciumfosfaat het hoofdbestanddeel van been), met een gewichtspercentage van 70 tot 80 procent naast de aanwezigheid van koolstof dat slechts 10 tot 20 procent van het gewicht uitmaakt. Dwarsdoorsnede analyses tonen aan dat een deel van de beenderzwart deeltjes hun zwarte kleur hadden verloren en er nu witig uitzien. De witte deeltjes fluoresceerden sterk in UV licht, terwijl het intacte beenderzwart er donker uitzag. Een ander opvallend kenmerk, dat naar voren komt uit de EDX analyses, is de adsorptie van lood en mangaan (als zouten of zepen?) door de poreuze beenderzwart deeltjes. Het lood en mangaan is oorspronkelijk afkomstig uit pigmentdeeltjes die aanwezig zijn in de zwarte la(a)g(en) of de onderliggende loodwithoudende grond. Daarentegen onthullen de EDX elementverdelingsschaartjes en FTIR beelden homogene verdelingen van fosfaat, fosfor en calcium in het intacte en wit geworden beenderzwart. Dus een omzetting van het calciumfosfaatsubstraat dat de kleurverandering had kunnen verklaren is niet aan de orde. Het lijkt aannemelijker dat het verkoelde organische materiaal in beenderzwart, verantwoordelijk voor de zwarte kleur, is weggereageerd in de aanwezigheid van lood (en mangaan). De omstandigheden waaronder het beenderzwart moet zijn gemaakt beïnvloedt de stabiliteit van het pigment. Het Röntgendiffractiepatroon van de
beenderzwart monsters onthult een amorf of laag-kristallijne hydroxyapatiet dat erop wijst dat het beenderzwart bij relatief lage temperatuur moet zijn bereid. Dit suggereert een lage kwaliteit beenderzwart of een opzettelijke gebruik van beenderbruin dat wordt gevormd bij onvolledige verkoling/carbonisatie.


In een aantal gevallen blijken de witte oppervlaktelagen gedegradeerde calciumcarbonaatrijke glacislagen te zijn, waarschijnlijk verouderde organische lakken, aangebracht over de donkere verflagen om modelering en speciale kleureffecten te creëren. Ze hoorden bij de oorspronkelijke laagopbouw. Vaak werden ook calciumoxalaten en loodchlorides aangetroffen in verband met de afbraak van deze kalkachtige lagen. Tot deze groep behoren: de wit geworden schaduwpartijen in de achtergrond van het Portret van een staande man door Rembrandt (1639, Staatliche Museen Kassel, inv. no. 239), de aangetaste donkere laarzen in de Triomfstoet met meegevoerde oorlogsbuit door Pieter de Grebber (1648, Oranjezaal, No. 24), het vergrijze oppervlak van de donkere mantel van de oude man in Salomon de Bray's Triomfstoet met veroverde wapenen (1649, Oranjezaal, No. 26) en de houtnerf-gerelateerde witte uitslag in het donkere interieur van Het vertrek uit de stal door Philips Wouwerman (1655-65, Mauritshuis, inv. no. 215).

In de andere gevallen kon de vorming van witte onoplosbare oppervlaktelagen worden toegeschreven aan migratieprocessen van lood en kalium door de verf heen naar het oppervlak, hoogstwaarschijnlijk in de vorm van zepen, waar ze reageerden met de atmosfeer en nieuwe stabiele minerale fasen vormden (w.o. carboxylaten, sulfaten, oxalaten, carbonaten). De witte afzettingen aan het verfoppervlak in de beschilderde plafonds van het Johan de Witt Huis (Den Haag, 1652-55) en die van de Oranjezaal door Pieter de Grebber, Frederik Hendriks hemelvaart (1650, No. 22) bestonden voornamelijk uit loodzepen en loodzepen gemineraliseerd tot o.a. loodsulfaat, terwijl de analyses van de oppervlaktelagen in Rembrandt’s Homerus (1663, Mauritshuis, inv. no. 584) en Het loftied van Simeon (1631, Mauritshuis, inv. no. 145), het Portret van Jacob Olycan van Frans Hals (1625, Mauritshuis, inv. no. 459) en de Tripenhuis plafonds beschilderd met jachtafereelen met luchten en vogels (Amsterdam, 1660-62) meer complexe korstsamenstellingen lieten zien. In deze laatstgenoemden, zijn naast
De mobilisatie processen worden gedreven door temperatuur- en vochtgradiënten, ten gevolge van bijvoorbeeld direct zonlicht, warmte en vocht geïntroduceerd bij bedoezing, of in één geval blootstelling aan warmte afkomstig van een brand. Robert Corkery heeft aannemelijk gemaakt dat metaalzepen in staat zijn zich te verplaatsen over waterfilms of zich bij verhoogde temperaturen makkelijk zouden kunnen verspreiden door de verf in de vorm van vloeibare kristallen. De reden voor de plaatselijke afbraak van de donkere partijen is in de eerste plaats te zoeken bij de verzeping van loodwit in de onderliggende (grond)laag en de samenstelling van de donkere verflagen. Het blijkt dat deze mediumrijke, poreuze donkere verven bijzonder gevoelig zijn voor de vorming van metaalzepen en hun transport naar het oppervlak. Omgevingscondities en mogelijk eerdere behandelingen kunnen dit proces van veroudering hebben verergerd. De korstsamenstellingen zijn niet statisch. In het begin waren ze grotendeels afhankelijk van de verfsamenstelling, terwijl in latere fasen de samenstellingen onder invloed van met name externe factoren moeten zijn veranderd. Aan het einde van dit hoofdstuk werden ook de gevolgen van de mobiliteit van metaalzepen voor de interpretatie van analytische data besproken, evenals de implicaties voor conservering.
Color changes and chemical reactivity in seventeenth-century oil paintings

geleid tot kleurveranderingen die een grote visuele impact hebben op het schilderij; de donkere partijen in het schilderij worden veel donkerder dan oorspronkelijk bedoeld. Dit is bijvoorbeeld geconstateerd in Orpheus betoverd dieren van Roelandt Savery (1627, Mauritshuis, inv. no. 157), waar de verdonkering van de bruine en grijze middentonen in de voorgrond heeft geresulteerd in een zichtbare verstoring van de oorspronkelijke licht/donker contrasten: de dieren verdwenen daardoor in de voorgrond, en de donkere voorgrond contrasteert nu te sterk met de lichte, blauwe lucht. Bijzonder interessant is ook het effect van toegenomen transparantie van het omliggende medium op de dekkingskracht en kleurintensiteit van andere pigmenten, zoals smalt in de verflag. Dit kon worden waargenomen in de ontkleurde luchtpartijen van de Tripenhuis plafonds beschilderd met jachtscènes met luchten en vogels (Amsterdam, 1660-62). De smaldeeltjes zien er transparanter en meer ontkleurd uit in een transparant bruine matrix waar al het loodwit is omgezet in zepen dan wanneer ze omgeven zijn door reflecterende loodwitdeeltjes.

Verlies van opaakheid komt ook plaatselijk voor. Onderzoek aan de panels van Aert van der Neer, Rivierlandschap (c. 1650, Mauritshuis, inv. no. 912), Jan van Goyen, Landvolk bij een vervallen boerderij (1631, Mauritshuis, inv. no. 1081) en Riviergezicht (c.1644-48, Mauritshuis, inv. no. 759), en Jan Steen, Dansende boeren bij een herberg (c.1644-48, Mauritshuis, inv. no. 553), onthult dat de verf op het poreuze vroege hout van de radiale zijde er donkerder uitzag in vergelijking met de naastgelegen verf op het late hout. Deze verdonkerde delen zijn het gevolg van plaatselijke loodzeepvorming in de loodwithoudende grond-/verflagen die gerelateerd blijkt met de dikte van de krijtgrondering, die de ongelijkmatige structuur van de houtnerf vult. De verdonkerde imprimatura schemert óf door de dunne, doorschijnende luchtlaag óf ligt bloot aan het oppervlak als gevolg van verflagverlies van de luchtlag door uitzetten van de verzeepde imprimatura. Dit heeft geleid tot een storend effect van donkere gestreepte lijnen op het schilderij. Afname van reflecterend vermogen van de krijtgrond door absorptie van oliecomponenten uit de verflagen (zoals aangetoond met massaspectrometrie) draagt ook bij aan het verdonkerings-effect omdat het licht hierdoor nog dieper in het schilderij/de verf kan doordringen. De aanwezigheid van olie in de krijtgrond verkleart ook de bron van de vetzuren die nodig zijn voor de omzetting van loodwit in loodzeep. Dat dit vaak wordt waargenomen in schilderijen op paneel uit het midden van zeventiende eeuw is techniek-gerateerd: niet alleen door het gebruik van grof generfd eikenhouten panels en loodwitrijke imprimaturalagen, maar ook door een voorkeur voor dunne, absorberende krijtgronden, eenvoudige verflagopbouw en open penseelwerk.

Dit soort veranderingen met betrekking tot de toegenomen transparantie en verdonkering van de olieverf door metaalzeepvorming heeft een grotere uitwerking op het veranderende uiterlijk van olieverfschilderijen dan vaak wordt aangenomen. Het blijft echter een open vraag hoe het kunstwerk weer opnieuw presentabel moet worden gemaakt, met name wanneer de verdonkering grote delen van het schilderij heeft getroffen. Hoe ver kan of wil men gaan met het retoucheren van zulke grote gebieden?
Dankwoord

Een proefschrift schrijven doe je niet alleen. Velen hebben mij hierbij geholpen.

Allereerst gaat mijn oprechte dank uit naar Jaap Boon, mijn promotor, en de AMOLF directie voor het creëren van de mogelijkheid om dit proefschrift te schrijven. Ik zie het als een mooie afsluiting van mijn onderzoeksbijdrage aan het De Mayerne programma (2002-2006). De gedachten en ideeën die zich ontwikkelden in de loop van de jaren met betrekking tot het schilderijonderzoek, en die zich in mijn hoofd opstapelden heb ik nu op papier kunnen zetten. Jaap, ik denk dat het een zeer productieve samenwerking is geweest. Ik heb voor mijn gevoel mijn eigen invulling kunnen geven aan dit proefschrift, maar jouw bijsturing en inzichten waren hierbij absoluut onmisbaar.

Het schilderijonderzoek op AMOLF binnen het De Mayerne programma gaf aanzet tot samenwerking met vele anderen. Dit maakte het onderzoek doen bijzonder stimulerend. Van mijn directe collega’s op AMOLF was de samenwerking met Katrien Keune heel bijzonder. Katrien, ik dank veel aan de talloze discussies die we in de afgelopen jaren hebben gevoerd. We raakten nooit uitgepraat, vooral niet toen we allebei nog dagelijks op Amolf waren, maar daarna gingen onze gesprekken gelukkig gewoon door. Veel ideeën in dit proefschrift zijn ontwikkeld tijdens deze gesprekken. De samenwerking met Petra Noble heb ik ook als bijzonder inspirerend ervaren. Deze vond plaats in het kader van de Open Laboratorium overeenkomst met het Mauritshuis. We hebben veel lange dagen doorgebracht bij de elektronenmicroscoop om weer nieuwe schilderijen monsters te bekijken en nieuwe ideeën te ontwikkelen. Veel van het werk dat hier is gepresenteerd is zeker ook jouw verdienste. Bovendien wil ik je nog extra bedanken voor de tijd die je hebt gestoken in het leesbaar maken van een aantal engelse teksten.

Het was heel fijn om weer samen te werken met Lidwien Speleers en Maartje Witlox, mijn oud-klasgenootjes van de restauratieopleiding bij de SRAL in Maastricht. Met Lidwien heb ik nauw samengewerkt in het Oranjezaal project. Maartje was betrokken bij het HART project. Ik wil jullie daarnaast allebei bedanken voor het grondig doorlezen van teksten voor dit proefschrift.

Ik dank ook veel aan de samenwerking met Edwin Verweij. Jij maakte het mogelijk dat ik ook zeventiende-eeuwse historische interieurs kon betrekken bij het onderzoek, hetgeen bijzonder nuttig bleek voor een beter begrip van een aantal processen, omdat die in interieurs vaak extremere vormen hebben aangenomen dan op de schilderijen. Bovendien wil ik je ook bedanken voor je hulp bij de infographics en lay-out van dit boekje.

Het uitvoeren van metingen aan schilderijen monsters vind ik altijd een spannende gebeurtenis, elk monster is anders dus je weet nooit van te voren wat je gaat tegenkomen. Ook op het analytisch-instrumentele vlak ben ik een aantal mensen veel dank verschuldigd met wie ik zo plezierig heb gewerkt. Jaap van der Weerd heeft mij met veel geduld en wijsheid ingewijd in de FTIR imaging techniek. Met Teun van Dillen heb
ik veel plezier gehad bij het werken met de SEM en hij heeft mij bovendien veel geleerd. Wat dat betreft heeft hij een uitstekende opvolger gevonden in de persoon van Hans Zeijlmaker. Jerre van der Horst wil ik graag bedanken voor alle DTMS metingen die hij voor me heeft gedaan, Jerre je bent een fijne collega en ik kon je gevoel voor humor altijd erg waarderen. I am also thankful for the opportunity to do Raman measurements with Silvia Centeno at the Scientific Department of the Metropolitan Museum New York, thank you Silvia for your time, it was fun and inspiring to work with you.

Natuurlijk wil ik ook de andere huidige groepsleden en oud-groepsleden van de schilderijen studies groep op AMOLF bedanken voor hun betrokkenheid en gezelligheid: Frank Hoogland, Nicole de Waal, Olga Katsibiri, Ester Ferreira, Beatrice Marino, Georgiana Languri, Tania Oudemans, Mark Clarke, Heleen Zuurendonk, Gisela van der Doelen en de onderzoekers van de groepen van Ron Heeren en Sander Piersma. I have also thoroughly enjoyed working with a number of guest researchers at AMOLF, especially Emily Gore, Ilaria Bonduce, Aviva Burnstock, Mark Richter, Ana and Stephan Schaefler and Rachel Morrison.

Ik heb de afgelopen jaren ook heel fijn samengewerkt met mijn andere Mauritshuis collega’s Sabrina Meloni, Carol Pottasch, André Jordaan, Barbara Schoonhoven, Maartje Witlox, de stagiaires van de SRAL, Johanneke Verhave, Vera Blok en Zeph Benders, and the interns from abroad, Alice Mohan, Linnaea Saunders (Kress Fellow), Alice Tate-Harte, once more Rachel Morrison; waarbij ik Jørgen Wadum speciaal wil bedanken voor de mogelijkheid om nog een dag in de week praktisch restauratiewerk uit te voeren, de betrokkenheid bij de schilderijenobjecten ervaarde ik als een extra impuls voor het onderzoek.

Ook de vele andere betrokkenen bij het De Mayerne programma wil ik graag bedanken voor hun bijzonder nuttige inbreng en feedback: Leslie Carlyle, Leslie your enthusiasm during the pigment meetings was always very encouraging; Prof. J.R.J. Van Asperen de Boer, hartelijk dank voor uw betrokkenheid bij het onderzoek en het beschikbaar stellen van schilderij monsters uit uw collectie; Yoshiko Shimadzu (ICN), Margriet van Eikema Hommes (ICN), Klaas-Jan van den Berg (ICN), Michiel Verhoeve (UL), Jaap Haasnoot (UL), Prof. Jan Reedijk (UL), Molly Faries (RUG), Astrid Smeets, Arie Wallert (Rijksmuseum), Annetje Boersma, en andere leden ‘Pigment Studies Group’ bedankt voor jullie inbreng. In addition, I would like to thank Ken Sutherland, Jo Kirby, Maarten van Bommel and Robert Corkery for their willingness to share their knowledge and ideas on specific topics.

Daarnaast wil ik deze gelegenheid ook aangrijpen om een aantal mensen in het bijzonder te bedanken die tijdens mijn opleiding tot schilderijenrestaurator aan de SRAL in Maastricht belangrijk voor mij zijn geweest. Anne van Grevenstein en René Hoppenbrouwer bedank ik voor hun grote inzet voor de opleiding. I owe especially to Helene Dubois (SRAL), Gwen Tauber and Laurent Sozzani (Rijksmuseum), and Mark Leonard (Getty Museum) who trained me in the ‘way of seeing into pictures’. Sometimes it is only afterwards that you realize how much you learnt.
Ten slotte wil ik mijn familie en al mijn vrienden bedanken die de afgelopen twee jaar zo met mij hebben meegeleefd bij het schrijven aan dit proefschrift, en wiens vriendschap en geduld ik voor mijn gevoel de afgelopen maanden/jaren danig op de proef heb gesteld. Het is moeilijk een goede balans te blijven vinden tussen werk en privé, hoog tijd om die weer te herstellen. Ik ben mijn ouders dankbaar voor hun onvoorwaardelijke steun en liefde, ik ben blij dat ik zo’n leuke zus en broer heb, Marieke en Joep, met wie ik het zo goed kan vinden en ook hun partners, Just en Astrid en mijn kleine nichtje Hannah. Ik vind het jammer dat mijn trotse oma dit mooie moment net niet meer heeft kunnen meemaken. Simone, ik ben blij dat ik je al zo lang ken en dat we zulke goede vriendinnen zijn. Hanneke, dank je wel voor je enthousiasme en dat ik altijd mijn verhaal bij je kwijt kan. En Edwin, ik wil je bedanken voor alles wat je me hebt meegegeven, en voor al je hulp bij de allerlaatste loodjes, fijn dat je er voor me was en dat we het met z’n tweeën konden doen. En dan zijn er nog velen die niet met naam en toenaam zijn genoemd.

Bedankt allemaal!
About the Author

Annelies van Loon was born in 1970 in Alkmaar, The Netherlands. In 1988, she obtained her VWO-B degree at the Murmellius Gymnasium in Alkmaar. She studied chemistry (Master of Science 1994, specialization inorganic photochemistry) and art history (Propedeuse 1994) at the University of Amsterdam. From 1995 to 2000, she was trained as conservator of paintings and painted objects (Postgraduate degree, specialization Old Master paintings) at the Limburg Conservation Institute (SRAL) Maastricht. She did internships at the Netherlands Institute for Cultural Heritage (ICN) Amsterdam (1998-1999), and the paintings conservation departments of the Frans Hals Museum Haarlem (1999) and the Rijksmuseum Amsterdam (1999-2000). She was advanced intern in the paintings conservation department of the J.P. Getty Museum Los Angeles in the period 2000-2001. Since 2001, she has been working as associate researcher in the molecular painting research group at FOM Institute AMOLF Amsterdam, where she was involved in the De Mayerne project MOLMAP funded by the Netherlands Organization for Scientific Research (NWO). In addition, she carried on with practical conservation work in the Mauritshuis studio. She conducted technical studies of seventeenth-century paintings of the Oranjezaal ensemble and the Mauritshuis collection with special interest into the material properties and deterioration processes. Part of the work is presented in this PhD thesis.