Color changes and chemical reactivity in seventeenth-century oil paintings
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Citation for published version (APA):

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Introduction

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 Tripenhuis, 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
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
Introduction

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.
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...
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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].

Microscopically

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\(^1\) 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.

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\(^1\) 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 CO\(_2\). The combined action of acetic vapors, CO\(_2\) 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).
(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 representation 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**


Introduction

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.
CHAPTER 2


CHAPTER 3


CHAPTER 4


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).
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Chapter 5


Other Publications


REFERENCES


Keune, K., 2005, ‘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.


