Color changes and chemical reactivity in seventeenth-century oil paintings
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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/schiery 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 Maurithuis 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
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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 Trippehuis 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 Trippenhuis 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 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 Trippenhuis 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.
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?