Color changes and chemical reactivity in seventeenth-century oil paintings

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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, ochre-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

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1 Except during World War II, when all paintings were moved to a bunker in Paaso 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).
Aging 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-
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High performance liquid chromatography (HPLC) was carried out to identify the dye components of the organic lake pigments.6 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. 2.1 Oranjezaal ensemble, 1648-1652, Huis ten Bosch Palace, The Hague. Photo: P. van Galen, RDMZ.

6 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.
7 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.
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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.
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,
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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

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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.9 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.10 The sizing layer on the canvas consists of pure animal glue.11 The grounds,
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{loottwit} rather than \textit{schulpwit} [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 [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 [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 [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. [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 (\textit{e.g.} \textit{m/z} 91, 105).
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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

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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].
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. 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 cm². 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). 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). Although its occurrence in seventeenth-century Dutch oil paintings has only been recently noticed, 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].

17 Generally, well-preserved smalt contains 10-15 wt% KO₂. In completely discolored smalt, KO₂ 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].

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).

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.

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, Gemäldegalerie Alte Meister [Stege et al. 2004] and more recently in works by Gerard Dou, *The Praying Anchoress*, 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.

21 There was an active peat industry in the Netherlands [Spring 2001, note 47].
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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 pulverant 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. 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 metavivianite, which has an intermediate composition, or alternatively to santabarbaraite, 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 polychromy sculpture, which have preserved their blue color and demonstrate a larger particle size. 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

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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: 4Fe^{2+}(PO_4)_3·8H_2O + 3O_2 → 4Fe^{3+}(PO_4)_3(OH)_2 + 26H_2O.

23 Metavivianite is a triclinic hydrated iron(II)-iron(III) hydroxy phosphate whose formula may be given as Fe^{2+}_{x+1}, Fe^{3+}_{x+1}(PO_4)_3(OH)_{(8-x)}H_2O 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 Fe^{3+}_{1/2},(PO_4)_3(OH)·5H_2O, 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.
The relationship between preservation and technique in the paintings of the Oranjezaal near Haarlem, where both De Grebber and De Bray lived. Interesting in this respect is the manuscript on painting technique and materials by Simon Eikelenberg, in which he describes a specific source in Alkmaar for vivianite, here called ‘blaù as’

source near Haarlem, where both De Grebber and De Bray lived. The term ‘Harlem’s Ultramarin’ is recorded by Richard Symonds in his notebooks of the 1650s (Spring 2003). It is also listed as ‘Haerlaems oltomarijn’ in the inventory from Trijntje 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).

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Fig. 2.13 Cross-section images of yellow fruit in Fig. 2.12 showing translucent metal soap aggregates in the lead-tin yellow paint.

Fig. 2.14 SEM backscatter image (BSE) and elemental maps (O, Pb, Sn) showing impurities of tin oxide in the lead-tin yellow pigment in Fig. 2.14.
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.
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.
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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). This appears to be a typical paint defect in lead-tin yellow paints [Noble et al. 2002; Higgitt et al. 2003; Keune 2005a]. 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, 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). 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 μm and 3 μm 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

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32 FTIR imaging showed a strong absorption band at c.1510-20 cm$^{-1}$ characteristic of the lead carboxylate group ν$_3$(COO). Many of the aggregates also contained lead carbonate as seen by a strong FTIR band at c.1400 cm$^{-1}$, assigned to the carbonate group, and a strong Raman band at 1052 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 λ= 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 cm$^{-1}$ (m) and c.525 cm$^{-1}$ (w) characteristic of lead-tin yellow type I, as well as a Raman shift at c.289 cm$^{-1}$ (s) attributable to massicot (lead(II) oxide) [Bell et al. 1997].
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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]. 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. 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. 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 μm 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 μm and 50 μm 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

Fig. 2.23 Detail of Salomon de Bray, Part of the Triumphal Procession with Musicians, 1649, Oranjezaal No. 26 (upper left), with microscope detail of the degraded surface of the shadow area of the red clothing of the child (upper right), and light microscopic and SEM backscatter images of a cross-section from the degraded paint. Photo (painting): Royal Collections. Photo (microscope detail): SRAL.

Fig. 2.24 EDX map of sulfur (left), FTIR image of sulfate group (center), and FTIR spectrum (right) of cross-section from the degraded paint in Fig. 2.23.
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.

Apparentely they found a good substitute in blue verditer, a synthetic basic copper carbonate (2CuCO₃·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

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38 The Raman spectra were recorded with a Renishaw System 1000 spectrometer using a laser with λ= 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\(^3\) 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).\(^4\) 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.\(^4\) Instead, Raman was more effective in identifying blue verditer in several cross-sections (Fig. 2.22).\(^2\) Blue verditer and azurite yield the same/identical spectra, which are different from green copper carbonates.\(^4\)

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.

\(^3\) Naturally formed spherical malachite also contains silicates, potassium aluminum silicate and sometimes dolomite, but these were not detected in our samples by SEM-EDX.

\(^4\) Strong FTIR absorptions at \(c.1415\ \text{cm}^{-1}\) and \(c.1490\ \text{cm}^{-1}\) from the carbonate group.

\(^2\) The Raman spectra were recorded with a Renishaw System 1000 spectrometer using a laser with \(\lambda = 514\ \text{nm}\). 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 Jordaeus’ Frederik Hendrik in Triumphi (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 \(c.403\ \text{cm}^{-1}\) that corresponded to the spectrum recorded of a blue verditer reference sample provided by the English Heritage, UK.

\(^4\) 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].
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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.
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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.
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**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

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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.\(^45\) 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).\(^46\) 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,

\(^{45}\) In most yellow lakes, some calcium salt is present. There are not many occurrences known of the use of yellow lakes containing alumina alone at this date. For instance, alumina-substrated yellow lake particles were detected in some of the dark paints in Rembrandt's *Aristotle with a Bust of Homer* (1653, Metropolitan Museum New York), see also Chapter 4, case-study of the *Homer* from the Mauritshuis collection.

\(^{46}\) See footnote 19.
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 to yellowing.

Fig. 2.28 Detail of Caesar van Everdingen, *Allegory on the Birth of Frederik Hendrik*, Oranjezaal No. 1, showing the degraded blue quiver (container for carrying arrows) (left). Microscope detail of the surface with very abraded ultramarine layer over grayed and degraded smalt underpaint (right). Photos: SRAL.

Fig. 2.29 Detail of Gerard van Honthorst, *Part of the Triumphal Procession, Amalia with her Daughters observing the Victory*, Oranjezaal No. 1. The blue dress painted with ultramarine has lost its modeling due to degradation of smalt in the underpaint. Photo: Royal Collections.
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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.\(^47\) 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.\(^48\) 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.\(^49\) 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

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\(^{47}\) 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.
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 Jordaeus’ 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.
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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.
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The herald’s jacket was found to consist mostly of resin, apart from some traces of oil.54 The use of a fast-drying resin may have been dictated by Van Couwenbergh’s working in situ.55 Finally, for smalt, there was no evidence of the use of media other than oil.

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

54 DTMS of the dark blue coat identifies a mixture of oxidized abietic acids (mass peaks at \( m/z \) 253, 271, 285, 301, 314, 315, 330), diterpenoid resins characteristic of pine resin. In addition, the spectrum shows traces of triterpenoid resins, aged mastic and dammar (\( m/z \) 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.

55 Van Couwenbergh painted the figures of the 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.

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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 Boschaaert'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.

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

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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 ≈ 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 ν(COO) and 1326 cm⁻¹ ν(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.\(^59\) 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).\(^60\)

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 (Hg\(_2\)S), 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, Hg\(_2\)Cl\(_4\) (calomel) and HgCl\(_2\). 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.\(^61\)

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)(AlSiO\(_4\))(SO\(_4\),S,Cl)).

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 *Triumphal 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 oil skin 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.

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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 28x19) 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 underpaint68, 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].

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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.
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ORPIMENT IN MIXTURES AND HIGHLIGHTS

Christiaan van Couwenbergh is the only painter in the Oranjezaal that used the pigment orpiment, a yellow arsenic sulfide (As₂S₃). 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.⁶⁹

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.⁷⁰ 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 (glass⁷¹; quartz; gypsum); both FTIR and DTMS identified the binding medium as pure oil.⁷² 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.⁷³ The layer structure of another sample, collected from the ochre-colored cuirass (breast armot) 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

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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 Asₙ₋₄ (n=1→4) and As₂Sₙ (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.
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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].
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