Color changes and chemical reactivity in seventeenth-century oil paintings
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Darkening as a result of Increased Transparency in 17th-C Oil Paintings

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

INTRODUCTION

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

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

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1 In addition to increased transparency, tiny craters filled with a whitish substance (corresponding to the phenomenon of metal soap aggregates) were observed [Van Eikema Hommes 1998: 118 and 2004a: 58; Wallert 1999: 94].
for fresh linseed oil compared to 1.57 for a very mature paint film). This was largely based on experiments in the 1920s and 30s by the British chemist A.P. Laurie [Laurie 1926]. However, for pigments with a high RI, such as lead white (RI: 1.9-2.1), this rise is not enough to explain the increased transparency observed in many paint films. Already in 1909, the German chemist Alexander Eibner, who was active with painting studies in Munich, suggested that increased transparency of lead white paints was a result of the formation of lead soaps [Eibner 1909: 121]. Gettens and Stout cite the work of Eibner in this regard [Gettens and Stout 1966: 175]. In 1967, Laurie admitted that the increase in transparency may in part be due to chemical change, also noting that when there is darker paint below, the picture will decrease in tone [Laurie 1967: 110, 140-155]. Rees Jones in 1991 calculated the effect of the age-induced increase in the transparency of oil paint, correctly observing that thinly painted pictures with a dark ground or underlayer are worst affected [Rees Jones 1991]. Townsend in 1993, pointed out that the change in refractive index is too small to account for the change in appearance and that it must be the RI of the pigment that alters, possibly as a result of a chemical change occurring on the surface of the particles from an interaction between the oil and the lead pigment [Townsend 1993].

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

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

Table 5.1  List of paintings examined

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

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

3 This build-up of ground layers is based on cross-sectional and elemental analyses of many panel paintings from this period in the collection of the Mauritshuis. This is proving to be in accordance with recipes for grounds from seventeenth-century documentary sources [Witlox & Carlyle 2005].
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- Jan Steen, *Dancing Peasants at an Inn*, (Mauritshuis, inv. no. 553), c.1644-48, oil on oak panel, 40 x 58 cm
- Unknown artist(s), Painted ceilings with hunting scenes with skies and birds, (Trippenhuis, Amsterdam, corridors and stairwells), 1660-62, oil on oak

**Experimental**

**Sample Preparation**

Samples were selected with the stereo-microscope and embedded in Technovit 2000 LC mounting resin, a one-component methacrylate that polymerizes under visible blue light (Heraeus Kulzer, Germany). Cross-sections prepared in the Conservation Studio of the Mauritshuis were made using *Easy Sections* (VWFecit, England) using Poly-pol PS230 polyester mounting resin with M.E.K.-peroxide harder (Poly-Service, Amsterdam). After initial grinding using silicone carbide (SiC) paper, the surface was dry polished using Micro-Mesh® Sheets (Regular type, grades 1500 thru 12000, Micro-Surface finishing products inc., Wilton, Iowa, USA).

**Instrumentation**

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

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Sample preparation was carried out by the Conservation Studio Mauritshuis.
Chapter 5

RESULTS

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

MICHAEL SWEERTS ‘DRAUGHTS PLAYERS’ 1652 (MH 1121)

In Sweerts’ Draughts Players, the yellow stocking of the right figure demonstrates an unusual patchiness owing to increased transparency of the paint (Fig. 5.1). The stocking is painted over a dark, almost black underlayer that is now shimmering through the partly transparent surface paint. A cross-section of a paint sample from a similar area painted with the same pigment, the yellow tassel of the stool on the left, shows the upper paint layer to contain lead-tin yellow $\text{Pb}_2\text{SnO}_4$ mixed with a little ultramarine and orange-colored earth pigment (Table 5.2; Fig. 5.2). In this sample, the reddish-brown earth ground, demonstrated in other cross-sections from the painting, are missing.

Light microscopic and SEM studies of the yellow layer demonstrate that the original lead-tin yellow paint consists of various heterogeneous phases. A large cluster of lead-tin yellow particles, visible at the left in the cross-section, as well as a few particles here and there throughout the layer (Fig. 5.2), exhibit the characteristic ochreish color in UV.

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5 This was noted during restoration of the painting carried out by Petria Noble in 2001-2002.
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and strong scattering in the backscattered electron images. Accordingly the EDX maps of these areas demonstrate the elements lead and tin (Fig. 5.2). For the most part, the layer, however, looks far from the normal homogenous paint layer consisting of opaque yellow particles. Instead the light microscopic image reveals many transparent regions that correspond to gray amorphous areas in the SEM backscatter mode having a lower lead density compared to the particles of intact lead-tin yellow having a high lead density.

6 Lead-tin yellow type I was established in a sample from the yellow stocking using X-ray powder diffraction. Analysis carried out by Arie Wallert, Rijksmuseum Amsterdam 2002 at the ICN [Wallert and De Ridder 2002: 45, note 32].
The affected layer also appears to have expanded. It is notable that no tin is detected in these gray areas, but rather only lead and large amounts of carbon (Fig. 5.2). The FTIR imaging data demonstrate dispersed lead soaps throughout the paint layer by the prominent absorption bands at 1509 cm\(^{-1}\) and 1403 cm\(^{-1}\) attributable to the lead carboxylate group, \(\nu_1 (\text{COO})\) and \(\nu_2 (\text{COO})\) (Fig. 5.2). Absorption peaks for the C-H bonds, typical of the aliphatic chain of the carboxylate, at 2941 cm\(^{-1}\) \(\nu_1 (\text{CH}_2)\) and 2854 cm\(^{-1}\) \(\nu_2 (\text{CH}_2)\) are also demonstrated. In earlier published studies of lead soap, protrusions/aggregates in lead-tin yellow paints, it was postulated that the excess lead oxide in the lead-tin yellow pigment, a lead-tin oxide (lead ortho-stannate), reacts with fatty acids released during drying/ageing of the oil medium to form lead carboxylates [Boon et al. 2004; see also section on lead-tin yellow in Chapter 2]. The selective reaction of lead with the free fatty acids can be explained by the fact that the tin(IV) oxide component is very stable and does not form carboxylates. The spongy, porous structure of the lead-tin yellow pigment that makes this pigment highly oil absorbent, explains the source of fatty acids available for saponification.

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

DARKENING OF MEDIUM BROWN AND GRAY TONES

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

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

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

8 Treated by Sabrina Meloni during internship in the Mauritshuis (SRAL intern 2002-2003) and documented in her final thesis [Meloni 2003].

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

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

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

\(^9\) In addition, the spectra contain longer chain fatty acids, C20FA-C26FA, at \(m/z\) 312-396.
of the pyrolysis products of the oil paint network is discernible with mainly aromatic components (e.g. \( m/z \) 91, 105).10

**Conclusion**

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

10 Furthermore, traces of pine resin (DHA at \( m/z \) 239, 287, 300 and OXO-DHA at \( m/z \) 253, 314, 315, 330) and mastic (at \( m/z \) 163 and 400-450 region) were detected, that are likely to be residues of old varnish.
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Fig. 5.4 Light microscopic images of cross-section from distant landscape (upper row), with corresponding FTIR images, EDX maps and SEM backscattered electron images. The saponified brown layer is the intermediate layer below the (green) top layer of the landscape. The white bands in the FTIR maps represent areas of high intensity.
Chapter 5

the color balance of the whole picture: the dark foreground now strongly contrasts with the light, bright blue sky, unintentionally creating a kind of dramatic chiaroscuro effect.\(^\text{11}\)

C. SELECTIVE DARKENING OF GROUND AND PAINT LAYERS ON THE WOOD GRAIN

Aert van der Neer ‘River Landscape’ mid-1650s (MH 912)

Loss of opacity is also observed associated with the wood grain on the radial surface of panel paintings creating disturbingly dark stippled lines that have often been interpreted as abrasion. In a panel painting by Aert van der Neer, dated mid-1650s - River Landscape-, many areas in the sky were found to be disturbed by dark lines that are associated with the wood grain in some way.\(^\text{12}\) Although they were also present in the darker areas of the picture, they were most disfiguring in the bright peach-colored sky. These streaks, which were found to correspond to the porous early wood on the radial surface, have become selectively more transparent and darker in tone, in contrast with areas of intact opaque paint on the late wood (Fig. 5.5). Examination with the stereomicroscope revealed that the streaks are formed in the underlying lead white-containing pinkish brown *imprimatura* that shimmers through the very thin sky paint or has become exposed as a result of loss of the sky layer.

In several cross-sections from the sky, three layers are present (Table 5.2): a chalk ground of variable thickness, a pinkish brown *imprimatura* (10-20 \(\mu\)m) and a single thin pinkish-grey sky layer (approx. 10 \(\mu\)m), consisting of lead white with the addition of a little vermillion, umber and glass (also carbon black in the grayer areas of the sky). In two cross-sections from the darkened lines, the *imprimatura*, which is essentially composed of large particles of lead white and a few large rounded particles of a relatively transparent red-brown umber (EDX: Fe, Mn, Si, Al, (Mg, K)), appears unusually transparent. Furthermore, small reddish umber particles are observed in these transparent areas (more Fe-rich than the browner umber particles) in close proximity to the brown umber particles. It is notable that in the samples from darkened areas a thick chalk ground is present (up to 60 \(\mu\)m thick), while in unaffected areas the chalk layer is thin or barely present. This difference in thickness of the ground is also apparent on the end grain (transverse sections) of the panels when viewed with the stereomicroscope. The ground fills the large pores of the vertical parenchyma cells of the early wood, which are huge in comparison with the smaller pores in the dense late wood (Fig. 5.6). Hence, we conclude that where the wood is porous (the early wood), the ground is thick because

\(^{11}\) From their composition, these middle brown- and gray-toned oil paints are very prone to darkening. A similar darkening process due to saponification of the lead white component may be responsible for the now dark areas in Raphael’s Transfiguration of Christ [Van Eikema Hommes 2004b], as well as in many other oil paintings.

\(^{12}\) The localized darkening in this picture was investigated together with Petria Noble 2002-2006. Treatment of the picture was carried out by Alice Mohan (Maîtrise de Sciences et Techniques (M.S.T.), University Paris I Panthéon-Sorbonne) during her three-month internship in the Mauritshuis 2002. The same phenomenon, though less visible, is present in Aert van der Neer’s *River Landscape at Sunset*, c.1650, (Mauritshuis, inv. no. 913).
it penetrated the cells opened by planning and sanding of the panel; where the wood is dense (the late wood), hardly any ground is present. The deep channels of the early wood can be clearly discerned on the back of the panel (Fig. 5.6). It is primarily these areas that become filled with ground during preparation of the panel. Dendrochronology concluded that the oak panel is of Baltic origin with an earliest felling date of about 1642.13

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

It is also noted that the chalk ground appears particularly porous. Binding medium analysis carried out with DTMS on an isolated sample of the chalk ground -from an area in the sky at centre right- suggests that the highly porous glue-bound ground has absorbed oil from the layer(s) above. In the mass spectra the signals for animal glue are almost obscured by the large amounts of oil derived components, the monocarboxylic and dicarboxylic fatty acids.14 The main mass peaks detected are m/z 256 and 284 from the molecular ions of palmitic and stearic acid, and m/z 152 a characteristic fragmentation ion of azelaic acid (C9 diacid). Only a small part of the fatty acids seems to be bound to the oil network, since the main fraction is released from the probe at low temperature (scans 25-40) indicating that they must be present in the free form [Keune 2005b]. The DTMS spectra also give evidence for the presence of chalk because of the release of CO₂ (m/z 44) detected at high scan numbers (scans 92-107) that is associated with the carbonate group from the chalk.

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13 Dendrochronology by Peter Klein, University of Hamburg, 2002.
14 Resin components, pine resin and dammar, identified with DTMS in the chalk ground, were probably introduced during past cleaning and varnishing. This indicates how absorbent/porous the chalk ground is.
Fig. 5.5 Aert van der Neer, *River Landscape*, c.1650 (Mauritshuis, inv. no. 912). Overall (inset) and detail of dark streaks in centre right sky (upper row); microscope detail (center left): light microscopic image of cross-section from dark streak (center right); SEM backscatter image of cross-section (912x10) from unaffected grey sky at upper right (lower left) and SEM backscatter image of cross-section (912x11) from dark streak immediately next to intact sample (sky layer is missing from this sample) (lower right).
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Fig. 5.6 Microscope detail of reverse of Aert van der Neer showing deep channels of the oak panel (left). Detail of the transverse section (end grain) showing chalk ground that preferentially fills the large cells of early wood (right).

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

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

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

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

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

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

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

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

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

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

Conclusion

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

Jan Steen ‘Dancing Peasants at an Inn’ c.1644-48 (MH 553)

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

Cross-sections were taken from a darkened line in the sky and from an intact (blue) area for comparison. The cross-section from the darkened area also includes two layers of blue overpaint that comprises modern cobalt blue pigment (a cobalt aluminum oxide, CoO₅Al₂O₃). Unfortunately, the ground and imprimatura layers are missing in this sample, since they crumbled during the sampling process. Like the other paintings under examination, this darkened area clearly correlates to the porous channels of the early wood that is filled with a thick layer of ground material. This is visible on the surface, in other darkened areas, where the surface paint is lost and the chalk ground that appears light brownish in color has become exposed. The cross-section from the intact blue area (see Table 5.2) shows the complete paint layer build-up: a chalk ground (up to 40 μm), a very thin light gray imprimatura (c.5 μm) and a single gray-blue sky

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

17 Analysis by FTIR of dark material collected from the deep porous channels of the early wood mainly showed peaks for cellulose from the wood, in addition to a little chalk. This implies that local shimmering of the panel through the upper paint layers that have become increasingly transparent also plays a role in the selective darkening.
Darkening as a result of increased transparency in 17th century oil paintings

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

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

**Conclusion**

The darkened lines in the painting can be explained by saponification of the lead white particles in the surface layers and very thinly applied *imprimatura*. The resulting loss of reflectivity of the paint and *imprimatura*, combined with the darkened chalk ground in these areas (from absorption of the oil from the *imprimatura*), permits the shining through of the panel in these areas. The results show that saponification of lead white is not restricted to the *imprimatura*, but can also affect lead white-containing surface layers, in this case, selective areas of the sky, as determined by the chalk ground that fills the uneven oak wood structure.
Fig. 5.11 Jan Steen, Dancing Peasants at an Inn, c. 1646-1648 (Mauritshuis, inv. no. 553). Overall and detail of dark streaks upper left sky (center left); microscope detail from figure in foreground (center right); SEM backscatter image of cross-section (553x04) from unaffected blue sky (lower left) and SEM backscatter image of cross-section (553x01) from overpainted dark line in sky (lower right) (same scaling).
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Fig. 5.12 Tripenhuis, painted ceiling N1, 1660-62 with detail of the discolored sky; detail of backscattered electron image showing saponification of the lead white, as seen by the gray halos (center right); light microscopic image of cross-section from discolored sky N1 (lower left) with corresponding SEM backscatter image (lower right). The browish areas in the cross-section correspond with low scattering, saponified areas in the SEM.
D. INCREASED TRANSPARENCY AND DARKENING (BROWNING) OF BLUE PAINTS CONTAINING SMALT AND LEAD WHITE

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

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

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

18 The ceilings are currently being restored by Edwin Verweij | Verweij Office for Architectural Paint Research and Conservation Amsterdam and Ruth Jongma | Bureau voor Kleuronderzoek en Restauratie Amsterdam.
**Conclusion**

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

**Discussion**

**Chemical and optical changes**

The reduction in opacity (i.e. increase in transparency) causing the darkening observed on the surface of the paintings presented can be explained by (partial) conversion of the lead white or lead-tin yellow pigment to metal soaps. From observation of the paint surface and the cross-sections, and as previously noted, it would seem that the smaller lead white particles first react away, leaving only the larger particles that are also clearly in the process of transforming into lead soaps. The opaqueness of lead white in oil is directly correlated to its light scattering ability. The transformation of lead white pigment particles to amorphous lead soaps will lower the light scattering ability and, instead, causes the light to penetrate deeper into the paint resulting in a darker appearance (Fig. 5.13). While a RI value for lead soaps has been assumed between that of the oil and the pigment [Robinet and Corbeil 2003: 24], recent measurement indicates a value close to that of the oil, 1.50-1.55.\(^{19}\) The gradual transformation of the lead white (or lead-tin yellow) particles to lead soaps significantly lowers the difference in refractive index between the binding medium and the pigment, leading to an increase in transparency. Moreover, any partially converted particles of lead white effectively become embedded in a high RI medium (the lead soaps) and thus appear transparent.

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

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

<table>
<thead>
<tr>
<th>Artist, title, date, support</th>
<th>Sample location</th>
<th>Paint build-up</th>
<th>Paint defect</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Increased transparency in lead-tin yellow paints</strong></td>
<td></td>
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<tr>
<td>Michiel Sweerts&lt;br&gt;Draughts Players&lt;br&gt;(MH 1121)&lt;br&gt;1652 canvas</td>
<td>Yellow tassel of stool, at left&lt;br&gt;1211x18</td>
<td>1. yellowish upper layer: lead-tin yellow, orange earth pigment, ultramarine (ground missing)</td>
<td>Saponification of lead-tin yellow in yellowish top layer resulting in a patchy, darkened appearance of the paint surface</td>
<td>LM&lt;br&gt;FTIR&lt;br&gt;SEM</td>
</tr>
<tr>
<td><strong>Darkening of medium brown and gray tones</strong></td>
<td></td>
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<tr>
<td>Roelandt Savery&lt;br&gt;Orpheus Enchanting the Animals with his Music (MH157)&lt;br&gt;1627 oak panel</td>
<td>Green landscape over brown background&lt;br&gt;157x36</td>
<td>4. green landscape layer: copper pigment, chalk, silicates?&lt;br&gt;3. brown background layer: lead white, carbon black, earth pigments&lt;br&gt;2. gray <em>imprimatura</em>: lead white, fine lamp black, little red&lt;br&gt;1. chalk ground</td>
<td>Saponification of lead white in medium brown background layer that has led to darkening of the layer</td>
<td>LM&lt;br&gt;FTIR&lt;br&gt;SEM&lt;br&gt;DTMS</td>
</tr>
<tr>
<td></td>
<td>Dark background&lt;br&gt;157x14</td>
<td>1. brown upper layer: lead white, carbon black, earth pigments (priming layers missing)</td>
<td>idem</td>
<td>idem</td>
</tr>
<tr>
<td><strong>Selective darkening on the wood grain</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aert van der Neer&lt;br&gt;River Landscape&lt;br&gt;(MH 912)&lt;br&gt;mid-1650 oak panel</td>
<td>Pink sky&lt;br&gt;912x05 (darkened)&lt;br&gt;912x10 (intact)&lt;br&gt;912x11 (darkened)</td>
<td>3. pinkish gray sky layer: lead white, little vermillion, umber, glass + carbon black in the gray areas of the sky (c.10 μm)&lt;br&gt;2. pinkish brown <em>imprimatura</em>: lead white, umber (10-20 μm)&lt;br&gt;1. chalk ground (up to 60 μm thick)</td>
<td>Darkening due to saponification of lead white in <em>imprimatura</em></td>
<td>LM&lt;br&gt;FTIR&lt;br&gt;SEM&lt;br&gt;DTMS&lt;br&gt;(ground)</td>
</tr>
<tr>
<td>Jan van Goyen&lt;br&gt;Dilapidated Farmhouse with Peasants&lt;br&gt;(MH 1081)&lt;br&gt;1631 oak panel</td>
<td>Gray-blue sky&lt;br&gt;1081x01 (darkened)&lt;br&gt;1081x02 (darkened)&lt;br&gt;1081x03 (intact)</td>
<td>3. gray-blue sky layer: lead white, (intact) smalt (10-15 μm)&lt;br&gt;2. light-gray <em>imprimatura</em>: lead white, chalk, little carbon black (10-20 μm)&lt;br&gt;1. chalk ground (up to 60 μm)</td>
<td>Darkening due to saponification of lead white in <em>imprimatura</em></td>
<td>LM&lt;br&gt;SEM&lt;br&gt;DTMS&lt;br&gt;(ground)&lt;br&gt;FTIR&lt;br&gt;(ground)</td>
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<tr>
<td>Jan van Goyen&lt;br&gt;River View&lt;br&gt;(MH 759)&lt;br&gt;c.1644-48 oak panel</td>
<td>Gray-blue sky&lt;br&gt;759x01 (darkened)&lt;br&gt;759x02 (darkened)&lt;br&gt;759x03 (darkened)</td>
<td>3. gray-blue sky layer: lead white, (intact) smalt (10-15 μm)&lt;br&gt;2. light-beige <em>imprimatura</em>: lead white, chalk, little umber (10-20 μm)&lt;br&gt;1. chalk ground (up to 60 μm)</td>
<td>Darkening due to saponification of lead white in <em>imprimatura</em></td>
<td>LM&lt;br&gt;SEM&lt;br&gt;DTMS&lt;br&gt;(ground)</td>
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Darkening as a result of increased transparency in 17th century oil paintings

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

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

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

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

Since there is no evidence in the documentary sources to suggest oil was added expressly to chalk grounds at this time22, we therefore have to conclude that the oil (and resin) components identified in the chalk/glue ground was most likely absorbed from the oil paint (and varnish) layers above. This was borne out of recent DTMS analyses of ground reconstructions comprising animal glue-bound chalk grounds covered with different types of oil-based imprimaturas. Here DTMS confirmed the absorption of oil components in the chalk grounds.23 The presence of oil in the chalk/glue ground also explains its lack of reflectivity and role in the localized darkening. Light can penetrate even deeper allowing the ground, and possibly also the panel, to shine through the transparent upper layer(s). In the four case studies presented here, the chalk ground has been deliberately applied very thinly, only filling the wood grain. In the darkened areas in the Van Goyen (River View) and Jan Steen, the lead white-containing imprimatura in the painting is also very thin, and seems to have been partly absorbed by the chalk ground thus explaining the loss of light reflectivity of the grounds in these paintings. Of course, it is difficult to know how reflective/absorbent the chalk grounds originally were, and indeed some chalk grounds appear more transparent and browner than others. In this sense, the thickness/porosity of the grounds is considered to be a decisive factor in the final appearance of paintings.

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

21 Acidic emissions or extracts from the wood do not seem to play a significant role in the darkening process as initially thought, since the thick chalk ground in the darkened areas would act as a buffer to neutralize acidic compounds.
22 Personal communication Maartje Witlox 2007.
23 Ground reconstructions were provided by Maartje Witlox and Tiarna Doherty 2007.
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Fig. 5.13 Schematic diagram showing the gradual dissolution and saponification of lead white in the upper paint layer and explaining the effect of saponification on the reflectance of light and on the surface appearance. Stages 1-5: (1) intact paint, light is scattered (2) early stage, first the small lead white particles react away, (3) mature stage, the small particles have reacted away, edges of the large particles are also dissolving, (4) late stage, the large particles are almost dissolved, (5) final stage, all lead white is saponified, light is absorbed.
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and shrinking of the thick chalk ground may have played a role in causing the surface paint to flake off in these areas exposing the darkened imprimatura. However, as already pointed out, a saponified lead white layer takes up a larger volume than it originally had;\(^\text{24}\) in this sense the physical expansion of the affected layer explains the paint loss associated with the early wood.\(^\text{25}\)

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

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

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

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

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

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

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

[translation by M. Witlox].

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

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

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

[Beurs 1692: 19-20]

Because of its great impact on the tonality and the long-term effects on the appearance of paintings, the nature of the ground attracts considerable attention in historical sources. In 1839 Henri Fielding refers to Van Goyen's (and others) use of transparent grounds as being 'the destruction of many fine pictures' stating that '...Van Goyen and others have prepared or filled up the pores of the wood with their transparent vehicle, which also enabled them to shew [original spelling] the grain of the wood through the shades of the subject'. [Fielding 1839: 81-82]. Even though Van Goyen made deliberate use of transparent grounds, it would appear that two centuries later, Fielding is referring to an increase in
the transparency of Van Goyen’s paintings due to the loss of hiding power in the priming and paint layers as has been described in this paper.27

CONCLUSION

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

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

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

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

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Chapter 5


