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SEM Backscattered-Electron Images of Paint Cross Sections as Information Source for the Presence of the Lead White Pigment and Lead-Related Degradation and Migration Phenomena in Oil Paintings

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Abstract: Scanning electron microscopy backscattered-electron images of paint cross sections show the compositional contrast within the paint system. They not only give valuable information about the pigment composition and layer structure but also about the aging processes in the paint. This article focuses on the reading of backscatter images of lead white-containing samples from traditional oil paintings (17th–19th centuries). In contrast to modern lead white, traditional stack process lead white is characterized by a wide particle size distribution. Changes in particle morphology and distribution are indications of chemical/physical reactivity in the paint. Lead white can be affected by free fatty acids to form lead soaps. The dissolution of lead white can be recognized in the backscatter image by gray (less scattering) peripheries around particles and gray amorphous areas as opposed to the well-defined, highly scattering intact lead white particles. The small particles react away first, while the larger particles/lumps can still be visible. Formed lead soaps appear to migrate or diffuse through the semipermeable paint system. Lead-rich bands around particles, at layer interfaces and in the paint medium, are indications of transport. The presence of lead-containing crystals at the paint surface or inside aggregates furthermore point to the migration and mineralization of lead soaps.

Key words: electron microscopy, backscattered-electron image, oil painting, paint cross section, lead white, lead soap, degradation, migration

Introduction

Scanning electron microscopy–energy dispersive X-ray (SEM-EDX) is an established and essential technique for the analysis of multilayer paint build-ups in cross section. The elemental analysis with EDX is used for the characterization of pigments and paint composition. Complementary information about the paint system is obtained in the backscattered-electron mode. The backscattered-electron image reveals the compositional contrast within the paint system. It highlights elements with high (appear light in the image) and low (appear dark) atomic weight, which is particularly helpful in the investigation of traditional paints, because the pigments used often contain high atomic weight elements, such as lead, arsenic, or mercury, that contrast sharply with the surrounding organic binding medium, that is composed of low atomic weight elements, such as carbon and oxygen. In this way, not only the individual layers, pigment particles, their shape, size, and distribution, and other paint constituents are visualized in paint cross sections, but also information about manufacturing processes and paint rheology is revealed, and insight is given in aging and degradation mechanisms in the paintings.

This article addresses the interpretation of backscatter images of paint cross sections with lead white pigment[a] and lead-related paint defects. A selection of various paint cross sections from 17th–19th century Old Master paintings will be discussed. Lead white plays a crucial role in traditional oil paintings and is used as the principal white pigment because of its high hiding power and its role in the drying of oil binding media. Lead white is vulnerable, however, to reaction with free fatty acids that are often released from the cross-linked oil in later stages of aging leading to mobile lead soaps, lead soap aggregates, lead-rich surface crusts, and the accompanying loss of hiding power.

For a full understanding of the paint defects as a result of the reactivity of lead white with binding medium components, several complementary analytical imaging techniques such as Fourier transform infrared spectrometer (FTIR) imaging and static imaging secondary ion mass spectrometry (SIMS) have been used in combination with SEM-EDX. In this article, the role of backscatter images in the illustration of lead white-related degradation processes is highlighted.

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[a]Lead white is a basic lead carbonate. Its composition is not uniform. Depending on the production and processing methods, it contains lead carbonate hydroxide [hydrocerussite, $Pb_3(CO_3)_2(OH)_2$] with various proportions of lead carbonate (cerussite, $PbCO_3$) and lead oxide carbonate hydroxide [plumbonacrite, $Pb_{10}(CO_3)_6(OH)_6O$].

Materials and Methods

Scanning electron microscopy studies in combination with EDX analysis were performed on a XL30 SFEG high vacuum electron microscope (FEI, Eindhoven, The Netherlands) with an EDX system with spot analysis and elemental mapping facilities (EDAX, Tilburg, The Netherlands). Backscattered-electron images of the cross sections were mostly taken at 20 kV accelerating voltage, at a 5 mm eucentric working distance and a spot size of 3, which corresponds to a beam diameter of 2.2 nm with current density of approximately 130 pA. Prior to SEM-EDX analysis, samples were either carbon coated in a CC7650 Polaron carbon coater with carbon fiber or gold coated (3 nm thickness) in a SC7640 gold sputter coater (both Quorum Technologies, Newhaven, East Sussex, UK) to improve surface conductivity.

Results and Discussion

Intact Lead White Paint

Lead white pigment is characterized by a wide variety of particle size and shapes depending on its production and processing method. Traditional lead white produced using the stack process[b] has a typical morphology, as is illustrated in a paint cross section from the white drapery (highlight) in Rembrandt's *Susanna* from 1636 (The Hague, Royal Picture Gallery Mauritshuis), which shows a white impasto paint composed of pure lead white pigment (Noble et al., 2005). The backscatter image demonstrates a dense layer with large lead white lumps and tiny lead white crystals filling the open spaces between the lumps (Fig. 1a). This very compact oil paint with a wide distribution of particle sizes has good standing properties and is therefore very suitable for rendering texture to the paint (Groen, 1997).

The paint cross section from *Susanna* was dry-polished in a polishing holder (method described in Van Loon et al., 2005). Small polishing marks are visible in the backscatter image (Fig. 1a). In addition, smearing of the embedding resin and/or paint sample masks part of the paint morphology. The importance of sample preparation for the quality of the images is demonstrated by another example of the use of high-quality stack process lead white (Fig. 1b). This sample is ion-polished, which has improved the surface quality and allows investigation at higher magnifications (Boon & Van der Horst, 2008). It shows a compact lead white ground (with small additions of umber, a brown earth pigment) that was used for the preparation of the 30 canvases for the Oranjezaal, a unique mid-17th century ensemble in the Royal Palace Huis ten Bosch, The Hague (Van Loon et al., 2006). The backscatter image illustrates that the large pigment lumps

[b]The manufacture of stack process lead white involves the placement of curled sheets of metallic lead in earthenware pots with little vinegar. These pots are "stacked" up surrounded by horse manure (that produces heat and carbon dioxide) and left for several months in a shed. The metallic lead is slowly converted into basic lead carbonate. This white corrosion product is scraped off, washed, dried, and ground (Gettens et al., 1993).

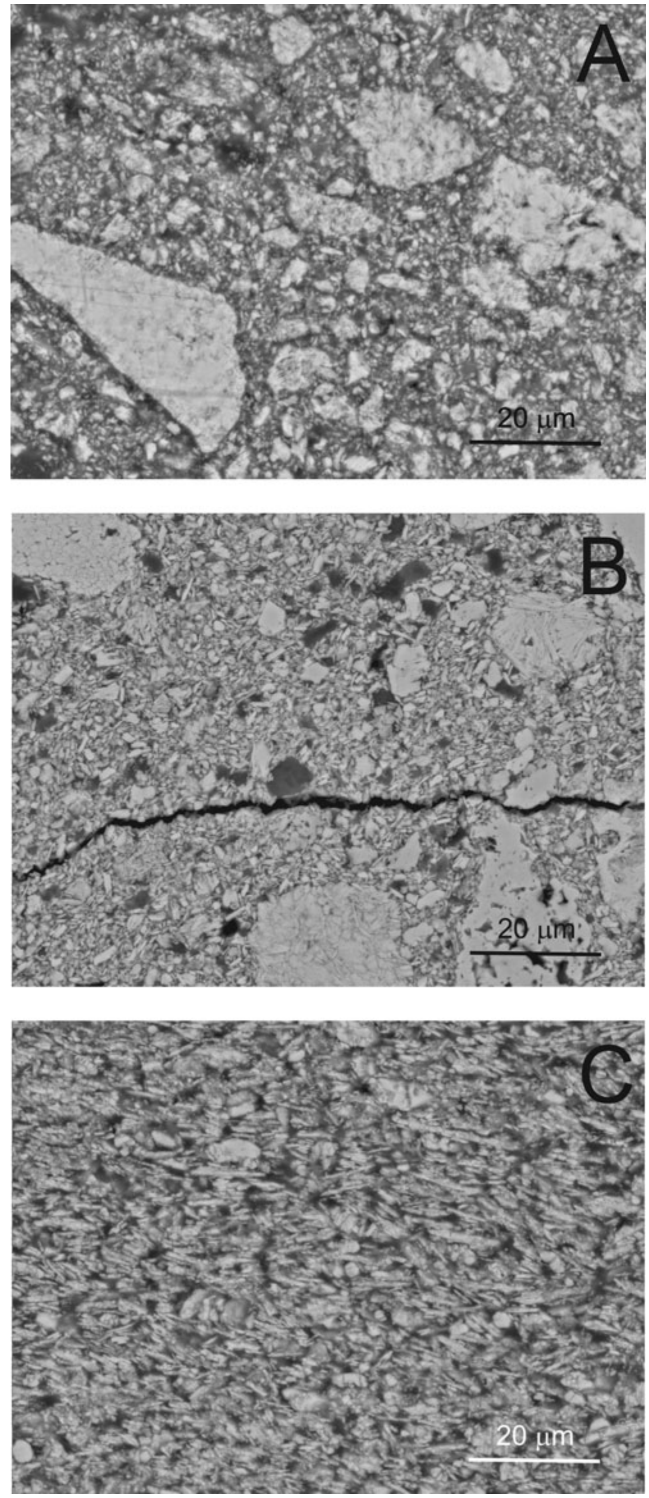

Figure 1. A: Backscattered-electron image showing hand dry-polished cross section of a compact stack process lead white impasto paint taken from Rembrandt's *Susanna* (1636), oil on oak panel, Royal Picture Gallery Mauritshuis, The Hague. **B:** Backscattered-electron image showing an ion-polished cross section of the compact stack process lead white ground preparation layer of the 30 canvases for the Oranjezaal ensemble (1648–1652) in the Royal Palace Huis ten Bosch, The Hague. **C:** Backscattered-electron image showing an oil paint reconstruction pigmented with modern lead white.

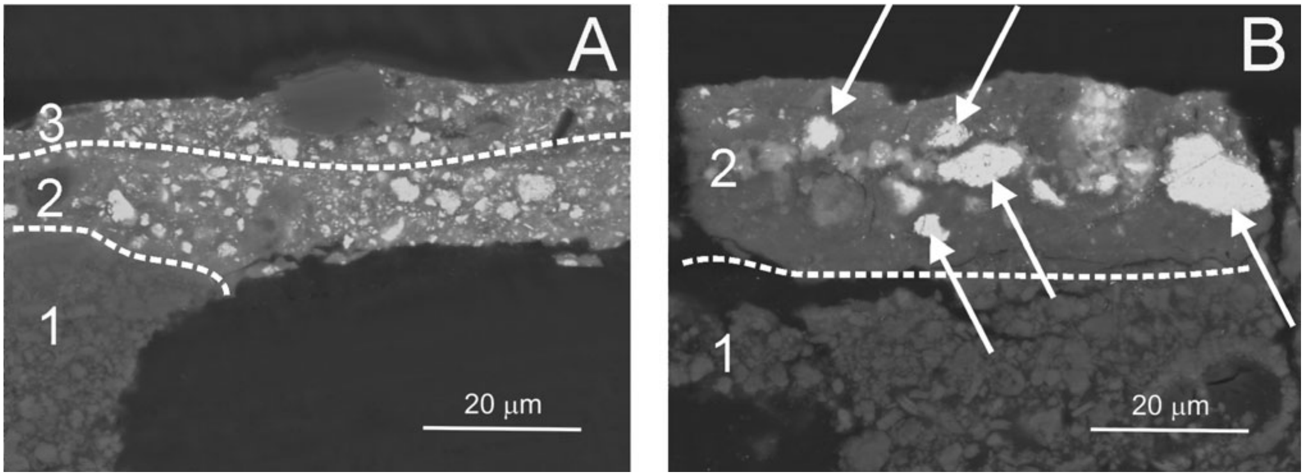

Figure 2. **A:** Backscattered-electron image showing an intact *imprimatura* paint with fine and coarse lead white particles (layer 2). **B:** Backscattered-electron image showing an affected (darkened) *imprimatura* paint with gray amorphous saponified areas and only a few coarse lead white particles (strongly scattering) left (indicated with arrows). Samples taken from Aert van der Neer's *River Landscape* (mid-1650s), oil on oak panel, Royal Picture Gallery Mauritshuis, The Hague. The layer build up: a chalk ground (1), *imprimatura* (2), sky paint (3) (missing in **B**).

are in fact dense conglomerations/clusters of submicron-sized crystal needles. They are comparable to the crystals that fill the interspaces, but the crystals in the lumps are more densely packed. Depending on their orientation, the crystals have an elongated or hexagonal shape in the backscatter image.

Modern lead white is distinctly different from stack process lead white in its particle size, shape, and distribution.[c] Figure 1c shows a backscatter image of a paint cross section from an oil paint reconstruction pigmented with modern lead white. While the historic lead white demonstrates a mixture of large and small particles, the modern lead white has a homogenous and narrow particle size distribution of elongated nonclustered crystals. These are mostly oriented and settled in the direction of the paint stroke. The particle morphology and distribution affect the paint rheology, handling quality, and visual properties of the paint. Furthermore, as shown by Carlyle (2006), modern lead white takes up twice the amount of linseed oil to achieve a workable paint compared to stack process lead white. This observation can also be explained by the difference in particle morphology as observed in the backscatter images of the two types of lead white, the stack process showing a higher packing density than the modern lead white.

Degraded Lead-Containing Paint

Dissolution of Lead White Particles

Paint defects related to lead soap formation are frequently recognized in lead-containing paints and can seriously affect the stability and appearance of the painting (Noble & Boon, 2007). Lead soaps are formed by the reaction between free fatty acids deriving from the oil and lead-containing pigments or driers. Free fatty acids migrate to the pigment surface, where the reaction takes place: the pigment particles slowly dissolve and can finally disappear. In this process, the smallest lead white particles will disappear first, while the coarser particles or lumps are still visible (but reduced in size). Evidence for this degradation process is found in the SEM images by affected particle edges, disintegrated particles, and/or lead-rich undefined regions. The saponified areas appear darker in the backscatter image than intact lead white due to their higher organic content.[d]

An illustrative example of the dissolution of lead white is found in the comparison of the *imprimatura* in two paint cross sections of *River Landscape* by Aert van der Neer (mid-1650s) (The Hague, Royal Picture Gallery Mauritshuis). The peach-colored sky in this painting is disfigured by dark streaks that are associated with the wood grain. One sample is taken from an unaffected area and the other one from a degraded, dark area in the sky (Noble et al., 2005, 2008). The sky shows a simple layer build up: a chalk ground just filling the wood grain (1), followed by a pinkish brown *imprimatura* containing lead white and a little umber (2), and a pinkish-gray top layer (3). The backscatter image of the unaffected area reveals fine and coarse strongly scattering, well-defined particles in the *imprimatura* (layer 2), typical for 17th-century stack process lead white (Fig. 2a). In contrast, in the *imprimatura* of the affected sample (layer 2), only a few coarse lead white particles (strongly scattering) are still visible, whereas the fine lead white particles have reacted away (Fig. 2b, the intact lead white is indicated with arrows). The gray (less scattering) peripheries around the large particles and the gray amor-

[c] Modern lead white is manufactured by faster production methods, e.g., via dry-process (Carter process), wet-process (French process), or electrochemical ("Sperry" process) methods.

[d] Additional analytical (imaging) techniques (FTIR/mass spectrometry) confirmed the formation of lead soaps (not discussed here).

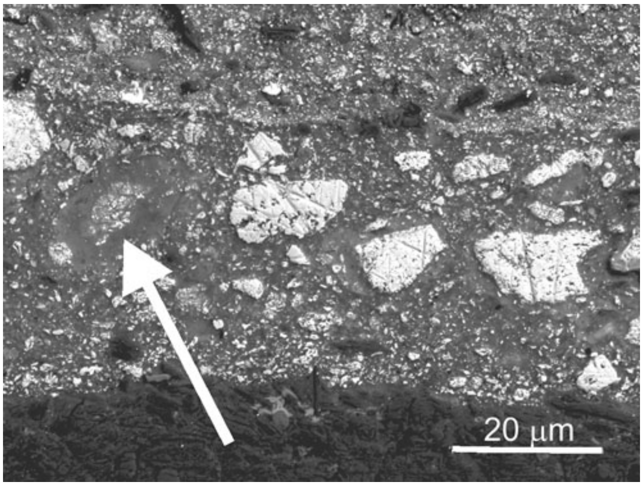

Figure 3. Backscattered-electron image showing the lead white-containing second ground with (partially) saponified lead white pigments (see arrow). Sample taken from Rembrandt's *Anatomy Lesson of Dr. Nicolaes Tulp* (1632), oil on canvas, Royal Picture Gallery Mauritshuis, The Hague.

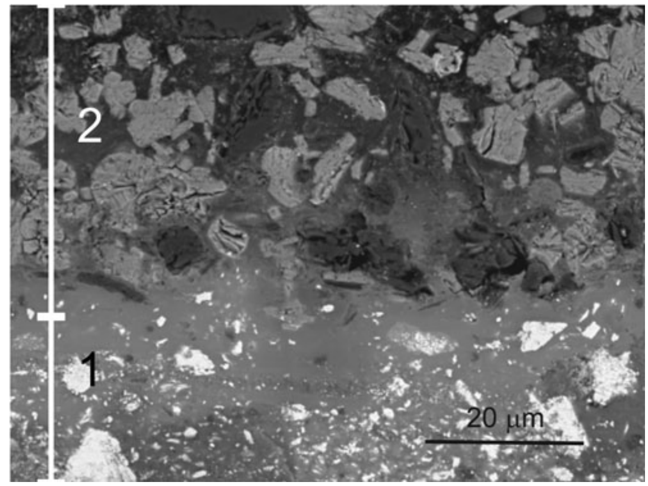

Figure 4. Backscattered-electron image showing the diffusion of lead soaps formed in the lower lead white paint (layer 1), which migrate into the upper Emerald-green-containing paint layer (layer 2). Sample removed from "Old-Holland table" (late-18th century) from "de Markiezenhof," Bergen op Zoom.

phous areas show that the original lead white pigment has dissolved and transformed into lead soaps.[e] These observations of the composition underneath the surface help to understand the visual changes observed at the paint surface. Lead white in oil has a strong light-scattering ability due to its high refractive index (2.7) thus making a very opaque paint, while the refractive index of lead soaps is near that of the oil medium (1.5). The saponification of lead white particles lowers their light-scattering ability and leads to an increase in transparency of the paint layer: the light penetrates deeper into the paint resulting in a darker appearance (Van Loon, 2008*a*). The darkened *imprimatura* (and underlayers) either shine(s) through the thin upper layer or is exposed where it has expanded causing the upper layer to flake off.

The transformation of lead white pigment into soaps is also visible in the second gray, lead white-containing ground of a paint cross section from Rembrandt's *Anatomy Lesson of Dr. Nicoleas Tulp* from 1632 (The Hague, Royal Picture Gallery Mauritshuis) (Fig. 3) (Keune & Boon, 2007). This layer is not as densely packed as the *Susanna* white impasto paint (Fig. 1a) or the Oranjezaal ground (Fig. 1b): the smallest particles appear to be dissolved. The grayish rims (of lead soaps) around the large pigment particles show that they are also in the process of dissolution (see arrow, Fig. 3). An interesting feature here is the disintegrated pigment lump at the left of the layer, surrounded by a gray halo, where free fatty acids have migrated inside the lead white lump structure and formed soaps.

Migration and Remineralization Processes

The previous section showed the potential of backscattered-electron images of cross sections in visualizing the reactivity of the lead white pigment particles with drying oil-derived constituents. The lead soaps that form, however, usually do not remain in place: they migrate or diffuse within the multilayered paint system (as liquid crystals), and precipitate and mineralize in the paint or at paint-air interfaces (along cracks or at the paint surface). The characteristic features of displaced and mineralized lead soaps in backscatter images will be discussed in this section. They manifest themselves as dispersed lead soaps/salts in the paint matrix, as aggregates or protruding soap masses, or as insoluble lead-rich crusts at the surface.

Paint is a semipermeable system: the transport of lead soaps seems to take place through organic-rich, interparticle, and low-density regions or along (nano-)pores and microcracks. These transport processes seem to be driven by gradients in temperature and moisture. Strong indication for the diffusion of lead soaps from a lower lead white-containing layer (layer 1) into an upper paint layer (layer 2) with Emerald green, for example, is found in a paint cross section taken from a late-18th century old-Holland table (Bergen op Zoom, "de Markiezenhof"). Figure 4 shows that a sharp interface between the two layers is missing. The upper part of the lead white layer (layer 1) is partly saponified as is demonstrated by the light gray amorphous areas (with carbon and lead detected as the only elements) and the low quantity of particulate lead white. These gray soapy areas are clearly integrated in the Emerald green layer indicating that the lead soaps are gradually diffusing into this layer.

Displaced or aggregated lead soaps usually crystallize or react with constituents from the paint or the environment forming new mineral phases such as lead carbonates, lead oxides, lead chlorides, lead sulfates, and/or lead potassium sulfates (Van Loon, 2008*b*). The newly formed products can be observed in the SEM images by their strong scattering

[e] Additional analytical (imaging) techniques (FTIR/mass spectrometry) confirmed the formation of lead soaps in this sample (not discussed here).

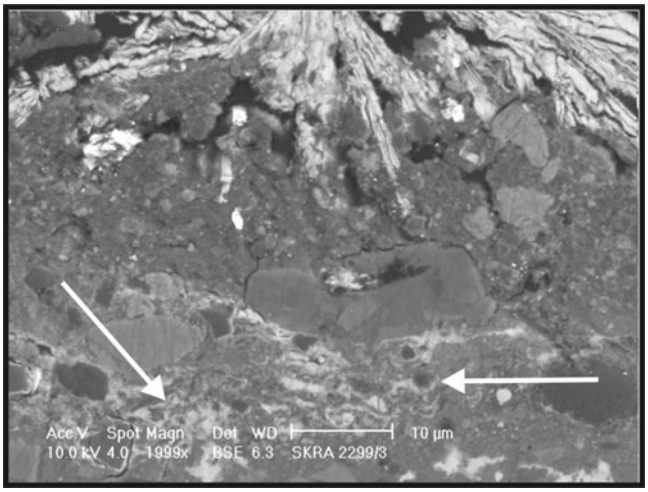

Figure 5. Backscattered-electron image showing lead soap crystals intercalated into the upper paint layer. The arrows indicate the lead-rich bands. Sample taken from Sigibert Chrétien Bosch-Reitz's *Portrait of P.J. Teding van Berkhout* (1891), oil on canvas, private collection.

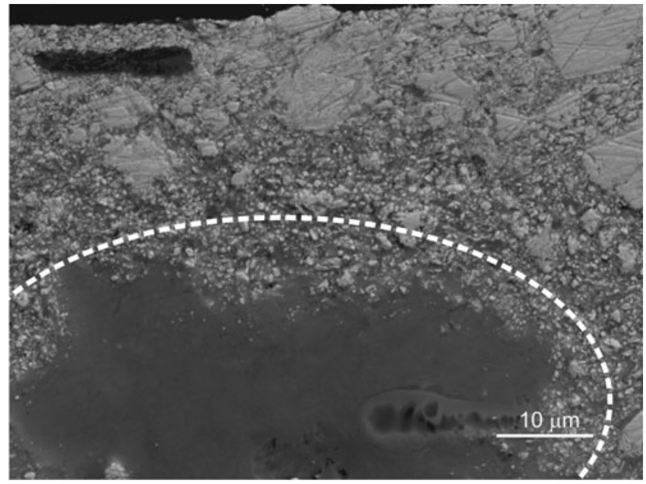

Figure 6. Backscattered-electron image showing lead soap aggregates in an early stage of development (indicated with dotted line). Sample taken from Rembrandt's *Anatomy Lesson of Dr. Nicolaes Tulp* (1632), oil on canvas, Royal Picture Gallery Mauritshuis, The Hague.

(they appear white or light gray) and their particle morphology that differs from the original lead-containing pigments. The oxide, chlorine, and sulfur counter ions of lead can be identified by EDX. Whitish crystals are clearly visible on the surface of the painting *Portrait of P.J. Teding van Berkhout* by Sigibert Chrétien Bosch-Reitz from 1891 (private collection) (locally varnished) (Keune et al., 2007). The SEM image of a cross section from the green background reveals lead-containing crystals fully integrated in the porous upper paint layer (Fig. 5). They appear light gray (strongly scattering because of the presence of lead) and have developed in lamellar structures. Lead soaps formed in the ground layer seem to have migrated toward the surface of the paint. Migration fronts, i.e., lead-rich bands, are visible in the paint matrix and around pigment particles (see arrows, Fig. 5). The largest part of the lead soaps, however, has accumulated at the paint surface, where they crystallized and/or formed new lead-containing compounds. The nature of this kind of surface deposits has implications for conservation treatment. Removal is not straightforward. The crystals are highly insoluble. In addition, the backscatter image illustrates that mechanical cleaning is not possible without removing original paint because the lead crystals at the surface are so intimately bound with the paint.

The last two examples address the phenomenon of lead soap aggregation: translucent masses form in the paint; they expand and can finally break through the paint surface resulting in gritty textures. This type of degradation is encountered on numerous oil paintings dating from different periods (Higgitt et al., 2003; Noble et al., 2003). The SEM images show the various stages in development. Figure 6 shows a backscatter image of the second gray ground in Rembrandt's *Anatomy Lesson of Dr. Nicolaes Tulp* (see also the discussion in the previous section and Fig. 3).

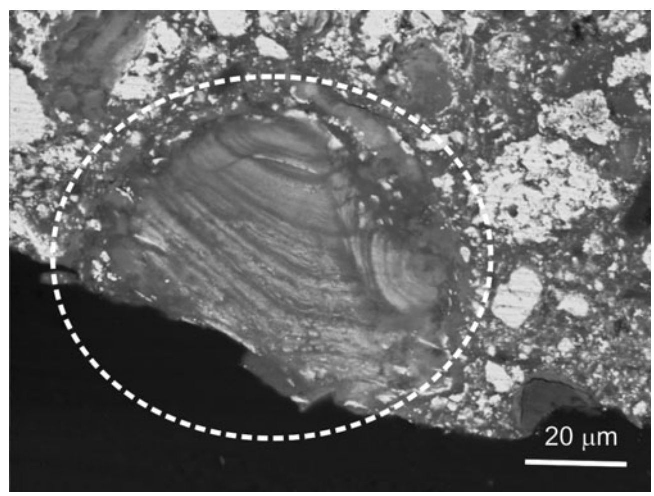

Figure 7. Backscattered-electron image showing lead soap aggregates in a more developed stage with lead carbonate-containing mineralization bands inside (indicated with dotted line). Sample from Christiaen van Couwenbergh's *Herald* (southwest) (1651), oil on canvas, Oranjezaal, Royal Palace Huis ten Bosch, The Hague.

A few small gray masses (low scattering) are visible in the partly saponified layer. The masses are identified as lead soap aggregates. They are in an early stage of development. A backscatter image of a more developed lead soap aggregate is displayed in Figure 7. This sample is from a green leaf in one of the *Heralds* by Christiaen van Couwenbergh, 1651 (Oranjezaal, Royal Palace Huis ten Bosch, The Hague). The soap mass has formed in the lower yellow layer containing lead white and lead-tin yellow. The lead soap mass has a shell-like striation pattern with bands enriched in lead (lighter gray in the backscatter image). The striations are interpreted as precipitation bands of a new lead compound (i.e., lead carbonates).[f] The newly formed lead carbonate does not develop into discrete particles and is therefore interpreted as a later formed precipitation product.

Conclusion

The case studies presented illustrate the detailed information concerning aging processes in the paint that can be deduced from SEM backscattered-electron images of paint cross sections. The traditional stack process lead white has a typical particle distribution of large and small well-defined particles that are highly scattering (i.e., appear white) in the backscatter mode. Changes in particle morphology and distribution, such as undefined pigments borders, unclear grayish areas, heterogeneous compositions, and unexpected particle shapes and sizes, are indications of chemical and/or physical reactivity in the paint system, here the dissolution of lead white, and subsequent migration and mineralization processes. This information can also be helpful for the interpretation of additional analytical data and in decision making for conservation and restoration treatments.

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[f] Imaging-FTIR identified lead carbonate inside the aggregate. This corresponds with the FTIR results carried out on paint cross sections with comparable lead soap aggregates with precipitation bands.