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### Delamination Due to Zinc Soap Formation in an Oil Painting by Piet Mondrian (1872-1944)

*Conservation Issues and Possible Implications for Treatment*

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Editors

# Metal Soaps in Art

Conservation and Research

Foreword by Taco Dibbits

 Springer

## Chapter 20

# Delamination Due to Zinc Soap Formation in an Oil Painting by Piet Mondrian (1872–1944)



## Conservation Issues and Possible Implications for Treatment

**Laura E. Raven, Madeleine Bisschoff, Margje Leeuwestein, Muriel Geldof, Joen J. Hermans, Maartje Stols-Witlox, and Katrien Keune**

**Abstract** The privately owned oil painting *Composition with Color Planes 4* (1917) by Piet Mondrian (1872–1944) has been the subject of ongoing investigation

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since 2011. The painting consists of color planes in a field of differing whites. Some of these white areas suffer from delamination issues, in combination with flaking. Previous research demonstrated a link between the presence of zinc oxide and the delamination phenomena. More recently, the formation of zinc soaps was found to play a role. In this study, cross sections from both delaminating and relatively intact white areas were investigated with light microscopy, SEM-EDX, and ATR-FTIR imaging to obtain more information about the stratigraphy and condition of the paint layers. Two stages in metal soap formation were identified in the delaminating areas. The first stage consists of noncrystalline zinc soaps or zinc ions bound to carboxylate functional groups in the polymerized oil network. Crystalline zinc soaps, which represent the second, final stage of metal soap formation, are generally linked to the development of zinc soap related deterioration phenomena. In this case, they were found at the interface between the delaminating paint layers. Possible implications for treatment and factors that might trigger further delamination will be discussed.

**Keywords** Zinc soaps · Crystalline · Non-crystalline · Delamination · Flaking · Piet Mondrian · SEM-EDX · ATR-FTIR · Treatment · Consolidant

## 20.1 Introduction

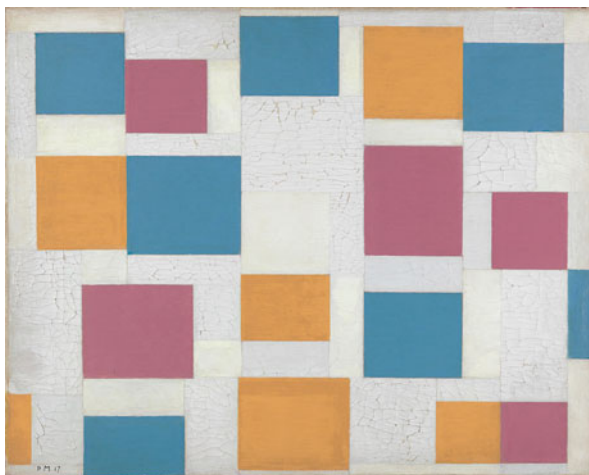
In 1917, Piet Mondrian (1872–1944) painted *Composition with Color Planes 4* (Fig. 20.1). The abstract composition consists of floating colored planes against a background of white planes in different hues. It forms part of a series of five works with a landscape format, of which four are painted on canvas (Joosten 1998).<sup>1</sup> All works in this series show similar compositions, but they vary slightly in color and in the arrangement of the planes. Mondrian worked on them in the same period, and all paintings are signed and dated 1917.

*Composition with Color Planes 4* belongs to a private collection. It is the only canvas painting within the series that for most of its lifetime has not been kept in a museum environment. Also unique to this painting is that it is the only painting that has neither been lined nor impregnated with wax or wax-resin, but it is also the only painting in this series that is currently showing delamination problems. Two of the three shades of white used in the final stage of the composition show severe cracking and flaking. We cannot exclude the possibility that the same alterations in

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<sup>1</sup>Private collection, *Composition with Color Planes 1*, 1917 (gouache on paper, 48 × 60 cm); Museum Boijmans Van Beuningen, *Composition with Colour Planes 2*, 1917 (oil on canvas, 48 × 61,5 cm, accession no: 1543 MK); Gemeentemuseum Den Haag, *Compositie No. 3, with Color Planes 3*, 1917 (oil on canvas, 48 × 61 cm, accession no: 0332897); Museum of Modern Art New York (MoMa), *Compositie No.5, with Color Planes 5*, 1917 (oil on canvas, 49 × 61,2 cm, accession no.: 1774.1967)

**Fig. 20.1** Piet Mondrian.  
*Composition with Color  
Planes 4*, 1917. Oil on  
canvas. 48 × 61 cm. Private  
collection. (Image courtesy of  
the owners and the  
Kröller-Müller Museum)



the paint are latent in the other paintings in the series, as they were created in the same period and possibly with the same materials.

Between 2011 and 2013, the condition of the painting led to in-depth research at both the Kröller-Müller Museum and the Cultural Heritage Agency of the Netherlands (RCE). At the time, it was suggested that drying cracks, in combination with loss of cohesion in an underlying zinc oxide containing paint layer had caused the paint to delaminate (Geldof et al. 2013). Condition issues relating to the use of zinc oxide are not uncommon (Osmond 2012; Mecklenburg et al. 2013); they have been noted in paintings by abstract expressionists such as Hans Hofmann, Franz Kline, and Jackson Pollock (Rogala et al. 2009, 2010, 2016; Maines et al. 2011).

In the case of the Mondrian painting, consolidation of the paint has proven to be very complicated, and it is the subject of ongoing discussion to this day. Softening and re-adhering the brittle paint has turned out to be difficult without risking further cracking or breakage. The paint film also seems to have slightly expanded (Bisschoff 2013). All this points to other factors being involved that appear to affect the painting's condition. The recently developed hypothesis that zinc soaps could play a role in the formation of the degradation phenomena in this painting gave a new impulse to this research.

In the past few years, the formation of zinc soaps has been receiving more attention (Osmond 2012, 2014a, b; Osmond et al. 2012, 2014; Hermans et al. 2014, 2015, 2016a, b, 2019). The relation between zinc soaps and structural instability of paint layers has been reported in another study on a painting by Mondrian (Van Loon et al. 2019) and, among others, in studies on paintings by Joan Miró, Jean Paul Riopelle, Jean McEwen, and Franz Kline (O'Donoghue et al. 2006; Maor and Murray 2008; Corbeil et al. 2011; Ebert et al. 2011; Helwig et al. 2014; Rogge and Véliz-Bomford 2015). However, the role of zinc soaps in the delamination of paint is still quite underexposed.

Little is known about how paint layers affected by zinc soaps should be treated. Brittleness of the paint is a common problem encountered during consolidation

treatments. The changing properties of saponified paint layers, however, pose new challenges to the conservator with regard to the effectiveness and long-term stability of consolidation measures. As stated, many twentieth century paintings already show problems related to zinc soap formation. As zinc oxide is still a common component of contemporary oil paints, a better understanding is needed to establish suitable active and preventive conservation methods.

The present study aims to investigate whether zinc soaps play a role in the delamination of the paint layers in two of the three white-colored shades used in *Composition with Color Planes 4* by Piet Mondrian. The results will be used as a basis to critically evaluate the suitability of current consolidation methods and to define parameters which conservators can take into account when dealing with similar delamination issues.

## 20.2 Experimental

To establish why delamination is occurring in some areas in the painting, it is important to understand how samples from affected areas differ from those taken in intact areas, and how this difference corresponds to what we see on the paint surface. Handheld X-ray fluorescence (XRF) analysis and the characteristic fluorescence of the paint surface in UV light already pointed toward a possible relation between the use of zinc oxide and the paint delamination in some of the white planes (Geldof et al. 2013). To confirm and understand the role of zinc oxide in the delaminating areas, three previously taken cross sections were reexamined: two samples (#3 and #4) taken from two different light-colored planes that show delamination and one sample taken from an intact white plane (#7).

To obtain a better understanding of the painting and its condition, visual and microscopic examinations were carried out. The paint layer buildup was investigated with optical light microscopy in dark field (DF) and ultraviolet fluorescence (UV). Scanning electron microscopy was used in combination with energy-dispersive X-ray spectrometry (SEM-EDX, both spot analysis and elemental mapping) to understand the morphology and stratigraphy of the samples and to determine the spatial distribution of the inorganic materials present. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) imaging provided more information about the internal conditions of the paint layers and the degree of change.

## 20.3 Results

### 20.3.1 Visual and Stereomicroscopic Examination of the Paint Surface

*Composition with Color Planes 4* consists of planes in six different colors, of which three are more brightly colored in dark pink, yellow, and blue. In some areas, it

can be seen that Mondrian toned down the brighter colors by repainting them, a technique that has also been observed in *Composition No. 3 with Color Planes* (van der Werf 1994). The white planes can be subdivided into groups according to the hue of their final layer, namely, bluish white, greyish white, and pure white.

When viewed in raking light, it becomes apparent that the delamination primarily affects the bluish and greyish white planes. In these areas the paint is cracking, cupping, lifting, and flaking, which has resulted in local paint loss. Two of the relatively intact pure white planes however also show flaking, indicating that the issue probably relates to the underlayers and not (solely) to the top layers.

Closer visual and stereomicroscopic examination of the painting shows that delamination is mainly occurring at the interface between a creamy or yellowy colored underlayer and the white top layer(s). This underlayer is not the first ground layer, but more likely a layer applied by the artist to cover up parts of an earlier composition. Piet Mondrian was known to frequently make changes in his compositions, and this painting is no exception (Blok et al. 2011; van der Werf 1994). Parts of an earlier stage of the composition are hidden by the frame rebate, and more compositional changes can also be observed in the X-radiograph. Consequently the stratigraphy of the paint is complex and may vary considerably from area to area.

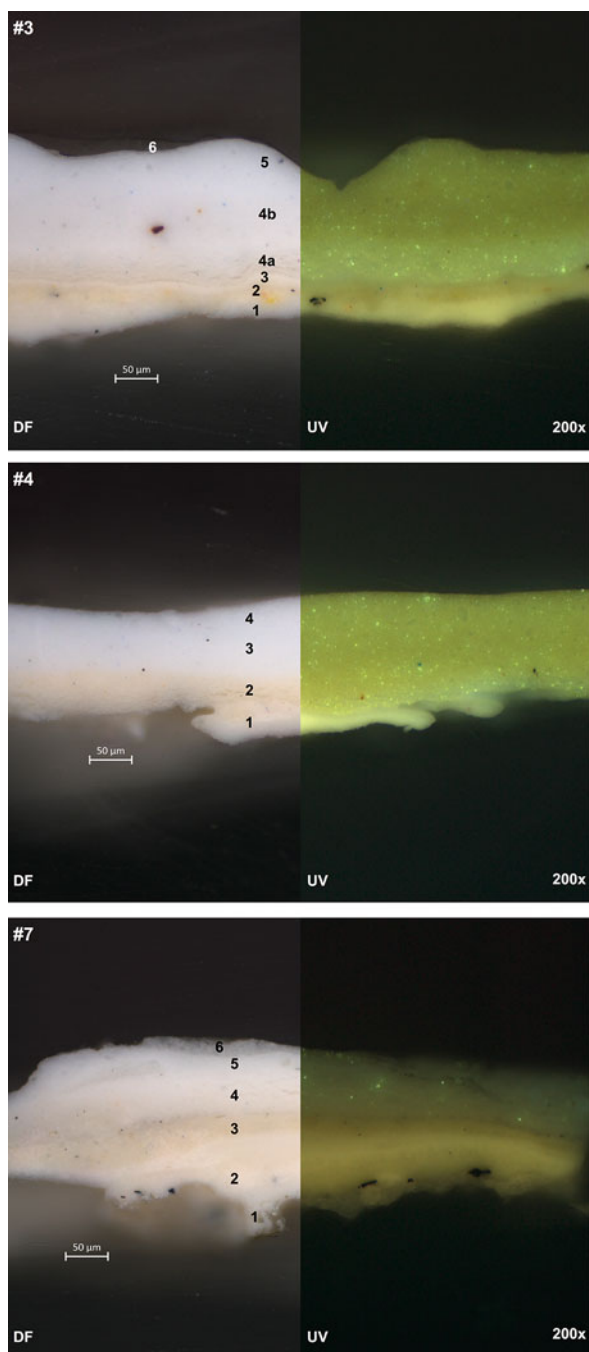
### 20.3.2 *Light Microscopy and SEM-EDX*

A thin white ground consisting of chalk in a drying oil was used to fill the interstices of the canvas (Geldof et al. 2013). SEM-EDX revealed that this layer was followed by the uniform application of a second ground layer that primarily contains lead. Depending on the area where the sample was taken, a third layer is present, which also comprises mainly lead. In sample #3, this layer is followed by a really thin (ca. 5  $\mu\text{m}$ ), densely pigmented lead white layer (Fig. 20.2, #3: layer 3).

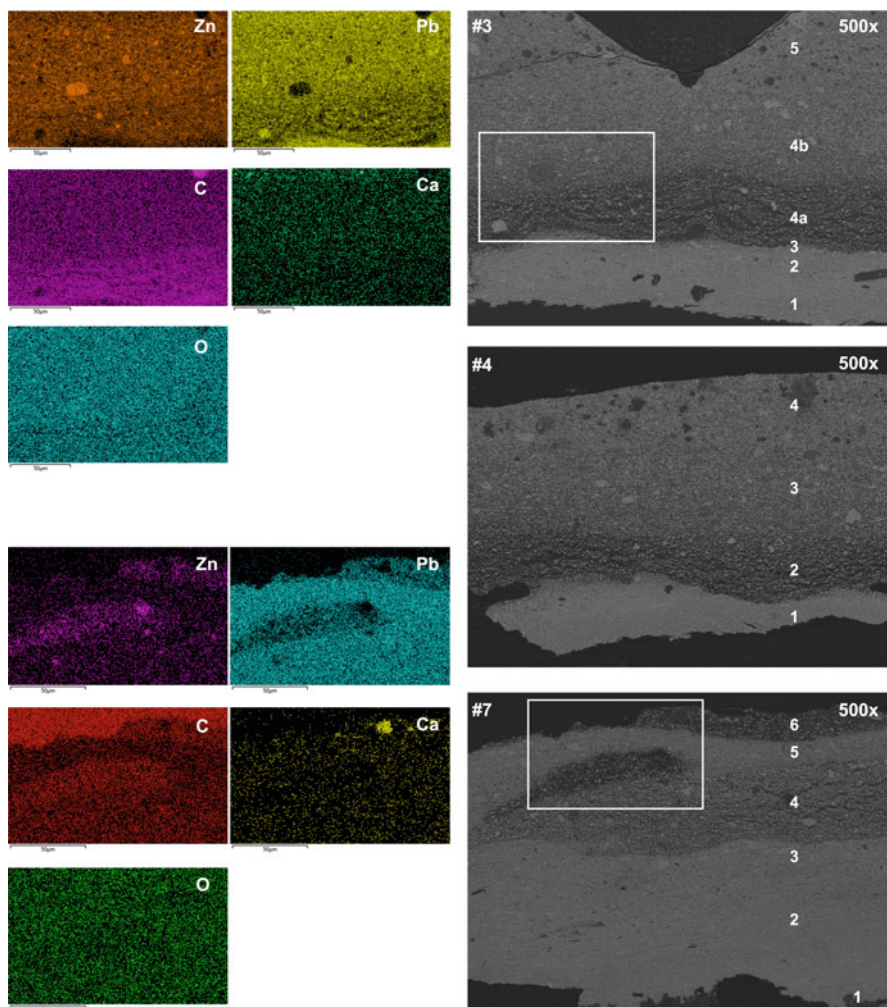
In samples #3 and #4, the lead layers are followed by multiple wet-in-wet applied layers, which consist primarily of zinc and lead white (Fig. 20.2, #3, layers 4a–4b; #4, layers 3–4). A small amount of an unidentified yellow pigment was found in the paint of the first layer in sample #4, hence its yellow color (Fig. 20.2, #4: layer 2). Elemental mapping reveals that the relative quantities of lead and zinc in this layer are comparable to that of the white layer above, which indicates a very similar overall chemical composition.

All samples look very similar in DF. In UV radiation however, the samples taken from delaminating planes look quite different from the sample taken in an intact paint area. Samples #3 and #4 show relatively more bright zinc oxide fluorescence than sample #7 (Fig. 20.2). This indicates a higher zinc content, which is confirmed by elemental mappings. In sample #7 the zinc content is lower than, for example,

**Fig. 20.2** Dark-field (DF, left) and ultraviolet (UV, 365 nm, right) light microscopy images of the cross sections. Magnification 200x. The main constituents were determined with SEM-EDX. Top: sample #3 (location, greyish white plane #18). Constituents: 1, lead white; 2, lead white, carbon black, and an unidentified yellow pigment; 3, lead white; 4a, zinc white and lead white. Part of layer 4b but is showing increased transparency; 4b, zinc white and lead; 5, lead white, zinc white, chalk, and ultramarine blue; 6, MS2A varnish layer. Center: sample #4 (location, bluish white plane #34). Constituents: 1, lead white; 2, zinc white, lead white, ultramarine blue, and an unidentified yellow pigment; 3, zinc white and lead white; 4, lead white, zinc white, chalk, and ultramarine blue; 5, MS2A varnish layer. Bottom: sample #7 (location, white plane #51). Constituents: 1, chalk; 2, lead white; 3, lead white and an unidentified yellow pigment; 4, lead white and zinc white; 5, lead white and zinc white; 6, lead white, zinc white, and ultramarine blue





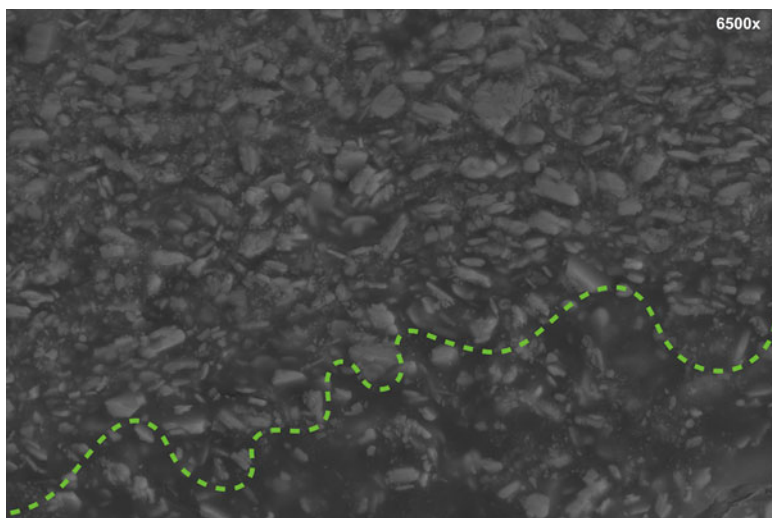


**Fig. 20.3** SEM-EDX elemental mappings of cross sections #3 and #7 (left): zinc (Zn), lead (Pb), carbon (C), calcium (Ca), and oxygen (O). SEM-BSE images (right) of cross sections #3, #4, and #7. Magnification 500×

sample #3, whereas the lead content is relatively high (Fig. 20.3). UV also reveals a faint fluorescence relating to an MS2A varnish (Geldof et al. 2013).<sup>2</sup>

When viewed with higher magnification, it becomes apparent that in samples #3 and #4, something is going on at the interface of a lead-rich layer and the first zinc

<sup>2</sup>No documentation is known for the conservation history of this painting. MS2A has been in use as a varnish since 1962 and must therefore have been applied during treatment after this date.



**Fig. 20.4** SEM-BSE image of detail layer 4 in sample #3. Magnification 6500 $\times$ . Above the green line, the zinc oxide particles are still visible in between the lead particles. In the lower area below the green line, where the fissuring takes place, there is hardly any zinc oxide left

oxide-containing layer (Fig. 20.3, #3, interface layers 4a–4b; #4, interface layers 1–2). The backscatter electron (BSE) images of these two samples reveal an area with lower electron density and lamellar fissures along the layer interface (Fig. 20.3). This phenomenon has previously been linked to the presence of zinc soaps, and it has also been noted in paintings by other artists such as Jean McEwen (Helwig et al. 2014). Elemental analysis revealed that this area is carbon rich (Fig. 20.3), which could be the consequence of saponification.

With higher magnification, a compositional change becomes visible in the area where the fissuring occurs (Fig. 20.4). Zinc oxide particles are still present in the upper part of the paint matrix, but there are hardly any detectable in the part where the fissuring is visible. The fact that there is a gradient instead of a clear border, and that there is an even distribution of lead particles in both areas, confirms that a conversion of zinc oxide particles is taking place in the lower part of the paint layer. This phenomenon can also be observed in sample #4. Similar fissuring is visible in the BSE image of sample #7, which was taken from an intact white plane (Fig. 20.3). It is remarkable that in this case, the fissuring is not occurring at the interface, but at the center part of the paint layer.

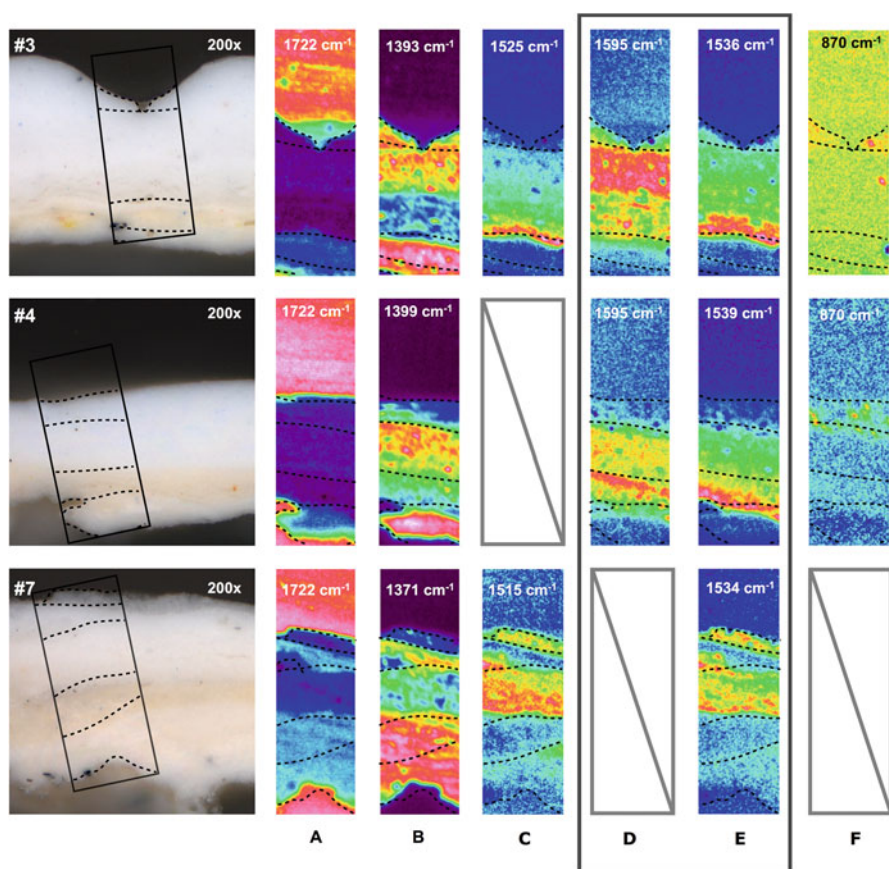
### 20.3.3 ATR-FTIR Imaging

Zinc oxide does not produce a spectrum in the mid-infrared range (4000–600  $\text{cm}^{-1}$ ) and is therefore not directly traceable in FTIR spectra. When mixed in oil, zinc oxide is, however, likely to produce a strong carboxylate absorption (Osmond

2012, 2014a). Recently, the existence of two different types of zinc carboxylate absorptions has been demonstrated experimentally. These have been linked to two different phases of zinc soaps (Hermans et al. 2015, 2016a, 2019).

A single sharp  $\text{COO}^-$  band around  $\sim 1536\text{ cm}^{-1}$  is characteristic for crystalline zinc carboxylates; in previous studies, it has been used to determine the presence of zinc soaps (van der Weerd et al. 2003; Shimadzu et al. 2008; Corbeil et al. 2011; Osmond 2012; Osmond et al. 2014). Noncrystalline zinc soaps however, as well as zinc ions bound to carboxylate moieties on the polymerized oil network (ionomer-like network), can be identified by a broadened asymmetric stretch  $\text{COO}^-$  band shifted to  $\sim 1570\text{--}1590\text{ cm}^{-1}$  (Hermans et al. 2016a, b).

Both zinc carboxylate vibration bands were identified in the zinc oxide rich paint layer in the samples from the delaminating white planes. ATR-FTIR mappings show that the crystalline zinc carboxylate band is present at the interface, where the paint layer is delaminating (Fig. 20.5). In samples #3 and #4, its spatial



**Fig. 20.5** ATR-FTIR imaging mappings of the three different samples: A, embedding medium; B, carbonate; C, lead carboxylate; D, noncrystalline zinc soaps; E, crystalline zinc soaps; F, chalk

distribution corresponds to the areas of lamellar fissuring visible in the BSE images. Interestingly, the upper part of the same layer, which shows the absorption band that is characteristic for noncrystalline zinc carboxylate (amorphous zinc soaps and the ionomer-like network), is better preserved.

## 20.4 Discussion

### 20.4.1 *The Role of Zinc Soaps in the Delamination of Composition with Color Planes 4*

Light microscopy and SEM-EDX examination showed that the samples from the delaminating paint areas, #3 and #4, have a relative high content of zinc white, whereas in sample #7, from the intact white plane, lead white dominates. The difference in pigmentation between the “delaminating” and intact samples, i.e., the zinc white and lead white ratio, plays a crucial role in the degree of zinc soap degradation resulting in delamination, as demonstrated in this case study. It is presumed that the free fatty acids are derived from within the layer and not from the lower lead white-containing layer (Kühn 1986). According to the BSE images, the lead white in the lower layer appears to be intact and unaffected by lead soap degradation. Therefore, we hypothesize that the fatty acids in this compact lower lead white layer are likely to be trapped by the lead and thus not able to migrate into the upper zinc white-containing layer.

The finding of vibration bands for crystalline and for noncrystalline zinc carboxylates within a single paint layer is quite remarkable, and for the first time, this can be linked to delamination issues.<sup>3</sup> The FTIR vibration band for noncrystalline zinc carboxylate is representative for the amorphous zinc soaps and the ionomer-like network. Unfortunately, it is not possible to distinguish between both types with ATR-FTIR.<sup>4</sup> However, it is likely that the ionomer-like network is homogenously distributed throughout the paint layer. As the noncrystalline zinc carboxylate dominates in the upper part of the paint layer, we can expect amorphous zinc soaps to be present.

Amorphous zinc soaps can be considered an intermediate stage and crystalline zinc soaps the final stage in zinc soap formation (Hermans et al. 2015, 2016a, b). A recent study into the crystallization process of metal soaps shows that amorphous, noncrystalline zinc soaps are inherently unstable and that they are able to crystallize spontaneously in oil (Hermans et al. 2016a). However, in a polymerized oil film,

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<sup>3</sup>The presence of two different types of zinc carboxylates within oil paints has been noted before but has never been linked to delamination. See Corbeil et al. (2011) and Szafran et al. (2014).

<sup>4</sup>Surface-sensitive techniques such as secondary ion mass spectrometry would be helpful to answer this question.

their potential to crystallize decreases due to changes in viscosity and chemical composition (Hermans et al. 2015, 2016a).

For the phase transition from noncrystalline to crystalline zinc soap in a polymerized oil network to occur, favorable kinetic conditions are needed that allow structural reordering of the carboxylate groups and aligning of the fatty acid chains. Temperature, water or moisture, solvents, and open spaces in the paint structure, such as (micro)-cracks, are likely to favor the packing of the fatty acid carboxylates (Hermans et al. 2016a).

In the Mondrian painting, it is possible that the formation of noncrystalline zinc soaps first caused the paint to delaminate, as a result of which the lower part of this layer could crystallize. Another possible scenario is that the noncrystalline zinc carboxylates crystallized, which then caused the paint to delaminate. The question at which point delamination occurred and whether the zinc soaps increased in volume during either of these scenarios is uncertain and requires further research.<sup>5</sup>

*Composition with Color Planes 4* was kept in an environment with uncontrolled climate conditions for most of its lifetime. The painting has been exposed to strong fluctuations and most likely high and low levels of relative humidity and temperature. The ability of the upper paint layers to respond to climatological changes was in all likelihood diminished by the loss of the unbound noncrystalline zinc soaps, which acted as plasticizers (Van Loon et al. 2012). One can imagine that when the flexible, mobile noncrystalline zinc soaps are converted into rigid and brittle crystallized zinc soaps, the paint film becomes less pliable and thus more prone to failure.

## 20.4.2 Consequences for Treatment

The existence of two types of zinc soaps and the notion that the degradation process is ongoing mean that standard approaches to consolidation have to be reconsidered, not only for the Mondrian painting but for all paintings that show zinc soap-related issues. Minimal intervention and compatibility of restoration materials to those that are original are two guiding principles for the consolidation of paint layers, especially since most consolidation treatments are irreversible by default. However, paint delamination due to zinc soap formation is most likely a continuous process. In the case of the Mondrian painting, it is feasible that new problems will arise when the noncrystalline zinc soaps in the part of the paint layer that lies above the consolidated area become crystalline. Ideally, a consolidant should be chosen that is capable of impregnating and consolidating both phases of zinc soaps. However, since the problem often concerns an underlayer, local treatment is quite difficult to achieve without impregnating adjacent layers.

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<sup>5</sup>Volume expansion has been observed in paints where metal soap aggregates have formed. See Keune (2005), Keune and Boon (2007), and Noble and Boon (2007).



It could be interesting to compare *Composition with Color Planes 4* with the other three canvas paintings in this series, which have been wax or wax-resin impregnated. Analytical research could provide insight into the condition of the paint structure and into the degree of saponification of the zinc white-containing layers, as well as the influence of previous treatments. This could provide valuable information with regard to the development of new treatment strategies.

### **20.4.3 Treatment or Risk Management?**

We assume that the development of zinc soap related damage is mostly dependent on the formation of crystalline zinc soaps. Much can be achieved by preventing the phase transition from noncrystalline to crystalline zinc soaps. The kinetics of metal soap crystallization are affected by several factors, such as the use of solvents, water, and heat. All have the ability to mobilize the fatty acid chains on the carboxylate groups, which can then reorder in an energetically more favorable arrangement and become crystalline (Hermans et al. 2016a). Awareness of this possibility is crucial, as all mentioned factors are regularly involved in consolidation treatments.

At this moment, to our knowledge, among the range of adhesives and consolidation methods currently available, not a single, suitable material and effective method can be found that fully negates all risk-increasing factors. In light of recent research, the question arises if the currently employed methods are still adequate, if not even potentially harmful. In order to safeguard potential high-risk paintings, it is important for conservators to be aware of the fact that their intervention might contribute to an acceleration of the degradation process.

Since an unstable climate is very likely to speed up the saponification and crystallization process, emphasis should be placed on preventive measures. High humidity levels will have a similar effect as water and allow more noncrystalline zinc soaps to form by releasing more free fatty acids through hydrolysis. It is presumed that the crystallization temperature of zinc soap drops below room temperature as the paint film becomes more polymerized (Hermans et al. 2016a). Chances for crystallization to occur are lower, if the painting is kept in a stable climate. Fluctuations will catalyze the saponification and crystallization process, as high temperatures will mobilize carboxylates, and low temperature levels will enable their crystallization.

This is of particular importance until more insight into the delamination process has been acquired, and innovative consolidation methods and materials have been developed. As previously stated, there is a need for a local impregnation method that enables the conservator to treat the zinc soap affected paint layers locally without having to affect the entire paint structure. In addition, the ideal consolidant should not contain solvents nor water and should work without heat activation.

## 20.5 Conclusion

With this case study, the presence of both noncrystalline and crystalline zinc soaps has for the first time been linked to serious paint delamination in an oil painting. The delamination occurs in specific paint areas that are rich in zinc oxide, and in the presence of free fatty acids, the highly reactive zinc oxide reacts to zinc soaps. The accumulation of crystalline zinc soaps at the interface where paint layers are detaching is responsible for the brittle nature of the paint. Noncrystalline zinc soaps, which have also been identified in what is chemically considered to be the same paint layer (Fig. 20.2, #3, layers 4a–4b; #4, layers 2–3), represent a first stage in the delamination process. The presence of two different phases of zinc soaps implies that further delamination is theoretically possible. This might compromise the long-term effect of consolidation treatments.

This research has helped to improve the understanding of the delamination processes due to zinc soap formation, which is a first step in finding a way to develop safer conservation strategies for paintings suffering from the described phenomena. A number of questions could be answered during this research, but many others still remain, which hopefully will be addressed by future research. In particular, whether the obtained results are representative for other paintings showing similar problems, and how this type of degradation may be influenced by treatment.

The question why in this case the zinc soaps formed at the interface with an underlayer is also still a subject of debate. In this regard, studies of other paintings with related problems, as well as comparing *Composition with Color Planes 4* to the other works in the same series, could give important clues. These matters are the subject of current research undertaken at the Rijksmuseum and the University of Amsterdam.

Reconstruction-based investigations could be useful to gain more insight into the mechanics behind the saponification process and how this can eventually lead to delamination. This could also provide more detailed information about the potentially harmful effects of agents such as water, heat, and solvents involved in consolidation treatments. This research is still ongoing, and we are optimistic that the knowledge gained can serve as a starting point for the development of safer treatments in the future.

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## **A.1 Appendix**

### ***A.1.1 Experimental Conditions***

#### **A.1.1.1 Embedding**

Samples were embedded in a polyester resin (Polypol) and dry polished with SiC polishing cloths (Micro-mesh<sup>®</sup>, final step 12.000 mesh).

#### **A.1.1.2 Light Microscopy**

All paint cross sections were examined under a Zeiss Axioplan 2 microscope, with both incident polarized light and incident UV light (from a xenon lamp and a mercury short arc photo optic lamp HBO, respectively). The UV H365 filter set used for examination in UV consists of the following filters: excitation BP 365/12, beam splitter FT 395, and emission LP 397.

#### **A.1.1.3 SEM-EDX**

Scanning electron microscopy in combination with energy-dispersive X-ray analysis (SEM-EDX) studies were performed on a Verion high-vacuum electron microscope (FEI, Eindhoven, Netherlands) with an EDX system with spot analysis and elemental mapping facilities (Oxford). Backscattered electron images of the cross sections were taken at a 20 kV accelerating voltage, at a 5 mm eucentric working distance and with current density of approximately 130 pA. Samples were gold coated (3 nm thickness) in an SC7640 gold sputter coater (Quorum Technologies, Newhaven, East Sussex, UK) prior to SEM-EDX analysis to improve surface conductivity.

#### **A.1.1.4 ATR-FTIR Imaging**

FTIR spectral data were collected on a Perkin Elmer Spectrum 100 FTIR spectrometer combined with a Spectrum Spotlight 400 FTIR microscope equipped with a  $16 \times 1$  pixel linear mercury cadmium telluride (MCT) array detector. A Perkin Elmer ATR imaging accessory consisting of a germanium crystal was used for ATR imaging.

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