Investigating Fluidizing Dripping Pink Commercial Paint on Van Hemert's *Seven*-Series Works from 1990–1995

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Abstract A painting from the *Seven* series by Frank van Hemert made between 1990 and 1995 was starting to show fluorescent exudates and drips after about 7 years. Paint samples were investigated with analytical mass spectrometry, solid state NMR, imaging FTIR and SEM-EDX. Fluorescent exudate of fluidised paint compared to rubbery paint underneath showed differences in FTIR and MS characteristics related to the distribution of polar acylglycerides with ester bonded and free azelaic acid groups. The oil in the Schmincke Norma Fleischfarbe nr 213 tube paint used by van Hemert consists mainly of semidrying oil giving a Drying Index of 72. Imaging FTIR identified aluminium soaps in fluorescent vesicles in the solid rubbery paint. Solid state NMR indicated that these aluminium soaps are degraded and consist mainly of aluminium hydroxy-monostearates. DTMS and ESIMS showed apolarity inside the rubbery paint compared to the exuding material. The drying of the paint produced high relative amounts of smaller oxidised fractions that could not be retained in the paint mass as aging progressed. A physical separation resulted in more polar fractions. The fluorescence of these exuding fractions can be used a tracer for failing or impending failing of oil paint.

Keywords Dripping paint • Failing aluminium stearates • Fluorescent exudates • Phase separation • Mass spectrometry (ESIMS • DTMS • GCMS) • Ester and non-ester bound organic fractions • FTIR-microscopy

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Introduction

Seven years after completion of the paintings from the *Seven* series (made between 1990 and 1995 by Frank van Hemert (Gemeentemuseum Den Haag 1996), the pink paints became tacky, the impasto developed a molten appearance, and began to form drips. Van Hemert used three paints for most of these works: a bright red toluidine oil paint, a dark alizarin oil paint and a pink oil paint, applied directly from the tube to the canvas, and further worked using a palette knife. The paints initially dried but the pink paint fluidised after about 7 years. In 2004 samples were taken for an initial study using mass spectrometry. (Boon et al. 2007; Hoogland and Boon 2007). Tube paint applied to a solid support in 2002 by paint chemist Pieter Keune was made available for analysis in 2004. The thicker impasto paint mass began to flow in 2009 and developed a molten appearance closely similar to that observed on the paintings. Drawdowns and the painting selected for analytical studies remained exposed to natural light until analysis in the present study.

The phenomenon of weeping paint and drip formation is of wider interest to artists, gallery owners and conservators as paintings by other artists show similar deterioration phenomena. In 2001, Duffy and McGlinchey reported dripping paint in a work by Jack Youngerman (Black, Red and White from 1962 @ MOMA). In 2003, Götz mentions in her Master thesis works by Matthieu, Soulages, Immendorf, Richter, Abello, Uhlig, Schultze, Dix and Hoehme with serious drying problems and fluidising paint. Schultz investigated in detail a so-called *fire*-painting *Harvest* (1993) by Otto Piene that started to show drips developing from a thickly painted impasto about 7 year after completion (Schultz 2011). More recently, we were contacted by Paul Walls, an artist in Northern Ireland whose white impasto paints started to drip after about 7 years. Paintings by the German action painter Meese have intentional drips resulting from his technique and unintentional drips that result from unstable paint, observed about 6–7 years after painting (Andreas Franz, 2013, personal communication).

Softening of post-1950 paints has been reported for Riopelle (Corbeil et al. 2004, 2011; Bronken 2010; Bronken and Boon 2014) who worked in France. Boon discussed and presented at the ICOP symposium a black oil painting by Soulages made in 1960 (Art Institute of Chicago) that is extensively weeping (Boon and Lister 2014). A poster at ICOP on a painting by G. Matthieu made with black tube paint in 1957 presented strong evidence of dripping paint (De Ségogne 2014). Many of the dripping paintings appear to be incidents related to poorly formulated paints, however the phenomena of softening and fluidizing oil paints may be part of a more general phenomenon that occurs in late twentieth and early twenty-first century paintings. Our rationale therefore is to contribute to the understanding of the mechanism of the undesirable softening and fluidisation of oil paints as the paintings age.

This paper reports many aspects of the dripping paints from the *Seven* series of works. An earlier version of a summary report (in Dutch) was provided to the lawyers of Van Hemert in 2010 for submission to the Court of Justice in Amsterdam where the artist is suing for damages. The studies performed at AMOLF and reported here are forensic art studies since no information was provided by the Schmincke Company about their pink paint for a long time. This paper characterises the visual qualities of a *Seven* series painting from 1992 and summarises highlights from a larger body of analytical information. A more detailed report on the MS and solid-state NMR studies will be published separately (Boon et al. in prep.).

Painting with Pink Paint Drips from the *Seven* Series

One painting made as part of the *Seven* series in 1992 (Fig. 1a–d) is the focus of the present study. The painting in Fig. 1a has a green wash with open spaces as background on the primed canvas. These open spaces were filled partially with a red wash and the numbers 1, 2, 3, 4, 5, 6. Drips from these washes are intentional. Thicker swatches of red, very dark brown and pink paint were applied as islands in/on the red washed areas directly from the tube. In other paintings from the *Seven* series, the same combination of the paints was used but the swatches are applied directly on the primed canvas. These paintings have the same problem of tacky

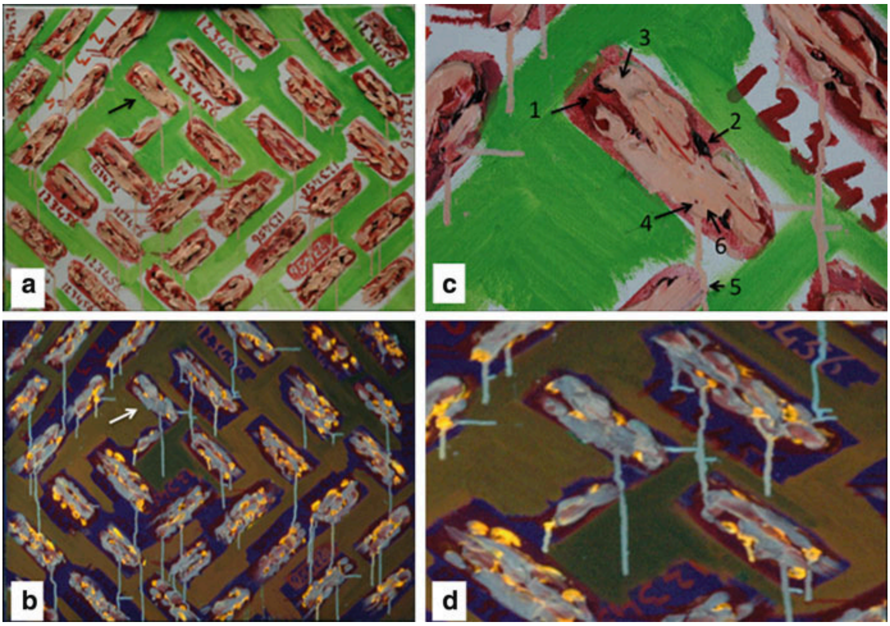

Fig. 1 Painting from van Hemert's *Seven* series made in 1992 that began to drip after about 7 years and photographed in 2005 (**a**). Exudate and drips are fluorescent under UV light (**b**). The *arrow* indicates the swatch that was chosen for sampling. The numbers in (**c**) (VIS) are the code used in the text for the paint and drip sample. (**d**) is the UV fluorescent picture corresponding to (**c**)

pink paints and drip formation. The stable toluidine red and dark brown alizarin paint were tube paints from Lefranc-Bourgois. The pink paint is Schmincke Norma Fleischfarbe nr 213 that the artist used in very large quantities from 1990 till 1995 when Schmincke took it out of production. The pink impasto paints show a molten appearance and drips were forming after a period of about 7 years. In some areas the pink paint drips dissolved some of the red paint. The reverse of these paintings shows a "wet" appearance where exuding medium has penetrated the canvas. This is often observed where the paint was applied more thickly to create the impasto effect. The surfaces of pink painted areas are still tacky and have attracted dust and fibers. Upon examination of the paint in cross section, it became apparent that the exuding fluids were highly fluorescent. Figure 1b, d show the fluorescence of the paints under UV light. The orange fluorescence is typical for the alizarin coloured dark brown paint (2 in Fig. 1c), which is still in the same place. The toluidine red paint (1 in Fig. 1c) is not fluorescent, and the bluish grey fluorescence is associated with the pink paint. Fluorescent exudate develops on the pink paint surface and drips develop when sufficient exudate has accumulated. All drips are connected to areas where pink paint was applied. The thickness of the paint ranges from less than 1 mm to about 5 mm. The relative amounts of dripping paint increased yearly thus increasing the length of some drips by 1–2 cm. Although not systematically investigated, the exudate production and flow increase seems associated with the relative humidity in the environment. The rate of flow increase was low in winter in the dry laboratory conditions of the AMOLF Institute, and higher in summer with a higher relative humidity. Samples of paint and dripping fluid were taken from one of the swatches in the center of the painting indicated with an arrow in Fig. 1a and b. Sample positions are shown in Fig. 1c with numbers and arrows. Pink paint was sampled near the top of the swatch (3) and lower areas (4 and 6) where the drip (5) had developed. Samples from the toluidine red (1) and dark brownish alizarin (2) paint were taken as reference of "normal" dried paint. Since the painter considered the painting a total loss, sufficient sample could be taken for multiple analyses. Remarkably, sample areas from pink paint "repaired" themselves after some time by plastic flow.

Figure 2a, b and c shows images from a remaining original Norma Fleischfarbe nr 213 paint tube used for the painting. A thin (<1 mm) and thicker layer (5–7 mm) of this paint was applied to a solid support in 2002 by the chemist P. Keune who made the paint tube and drawdowns available for analysis in 2004. Samples were taken from the middle of the paint tube, which was opened for that purpose with a scalpel knife and resealed. Photos of the drawdowns were taken in 2005 (Fig. 2b) and 2010 (Fig. 2b). At the end of 2009 about 7 years after making the drawdowns, drips had formed from the impasto paint, which itself also began to show a molten appearance. Samples of the drips were taken in 2010 to compare their MS features with those from 2005. The drip was found to be fluorescent under blue LED-light. The thinly applied layer was not tacky but showed a thin 1 mm wide rim of fluorescent material all around its circumference.

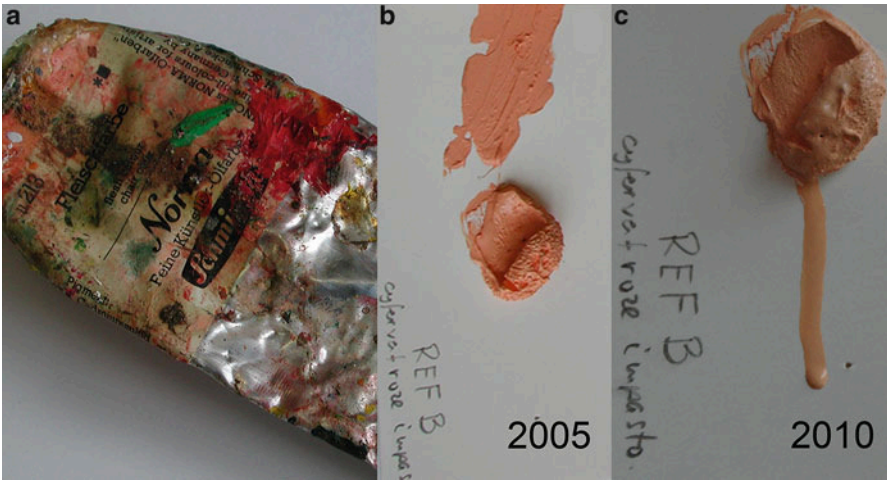

Fig. 2 A tube of Norma Fleischfarbe pink paint (**a**) used by van Hemert for his *Seven* series paintings. The paint was used in 2002 for thin and thick paint application (**b**) on a nonpermeable support (Photos were taken in 2005 and 2010). In late 2009 the thicker impasto swatch (**c**) showed a molten appearance followed by drip formation

Cross Sectional Analysis of the Pink Paint

The pink paint samples were too soft for regular embedding and polishing. Paint from position 4 could be embedded in Technovit LC2000. The resin block was sectioned with a glass knife microtome at a temperature of 5 °C to obtain an about 10 µm thick thin-section of the paint. This section was placed in a diamond cell for imaging FTIR and light microscopy. The remaining embedded section surface was further polished using Argon ion polishing at low kV and examined with light microscopy, SIMS and SEM-EDX to investigate the nature and distribution of pigments, extenders and organic constituents. Figure 3 is a backscatter electron (BSE) image at 16,000 magnification showing tiny rounded particles of Titanium white (EDX Ti, O), high intensity BSE aggregates of Cadmium red (EDX Cd, Se) and Cadmium yellow (EDX Cd, S) and rather fluffy darker grey irregular masses of calcium containing material (EDX Ca, C, O) with a low BSE intensity. The irregular aggregates are relatively large compared to the Titanium white particles. The dark low BSE intensity areas between these particles correspond to binding medium, which is present in relatively thick layers around these particles. This composition correlates well with data from a sample of the pink Norma Fleischfarbe tube paint and one from the 1992 painting analysed with XRD at the University of Amsterdam (Sonneveld 2006). The relative amounts estimated without calibration from the XRD data were 30–50 % Titanium white (rutile form), 40–60 % calcium carbonate, 5–10 % cadmium pigments and <2 % unexplained.

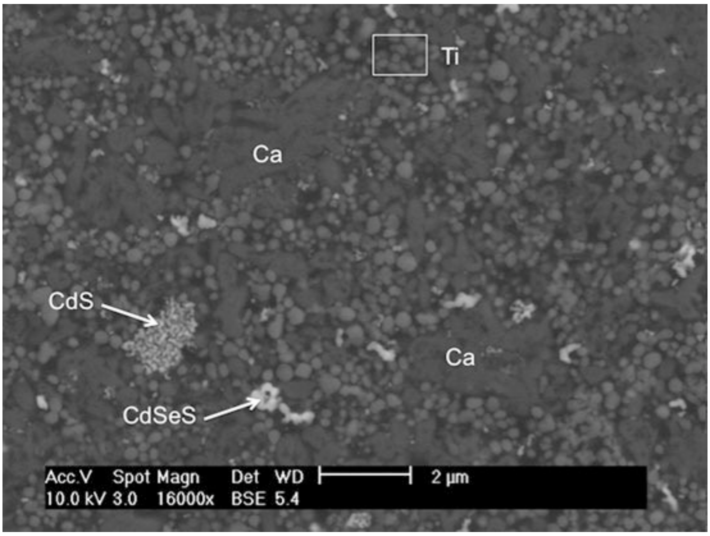

Fig. 3 Scanning electron microscopic image taken under back electron conditions at 16.000 magnification using a FSEM instrument (Fei XL30). The surface was obtained by microtoming and subsequent Argon ion polishing using a JEOL CP system

The thin-section of the pink paint from sample position 4 was investigated with light and FTIR microscopy in reflection and transmission mode. Figure 4a, b illustrate the more yellow-orange visible (A) and more pink-red UV-fluorescence (b) image of the paint. The top layer of the paint shows a bluish fluorescence. Smaller and bigger fluorescent vesicles are seen in the paint mass. Large Cd-yellow pigment particles show a reddish fluorescence. The red and blue squares indicate the areas that were imaged with FTIR microscopy. The corresponding FTIR images in Fig. 4c–e and f show the image maps of the CH asymmetric stretch vibrations of aliphatic chains (of fatty acids) at 2,920 cm^{-1} (c), the asymmetric C=O (carbonyl) stretch vibration at 1,740–1,780 cm^{-1} of ester bonds (acylglycerols) (d), of 1,610–1,630 cm^{-1} interpreted as C—O—C=C (vinyl ether) bonds (Colthup et al. 1964) (e), and 1,470–1,540 cm^{-1} specific for the CO_3 asymmetric stretch vibration in calcium carbonate (f). The images are false coloured from red via yellow and green to blue representing a gradient in relative concentration from high to low. The imaging FTIR methodology and interpretation has been described by Van de Weerd et al. (2005). The surface layer (marked 1) has a lower relative concentration of calcium carbonate, which is an extender in the paint. Higher relative amounts for aliphatic and ester moieties, and CH chains with a vinylether-bonded system are present in the top layer 1. The enrichment points to a compositional difference between top layer and the main paint mass (bulk). The FTIR image maps for the red lined area in Fig. 4g–i were derived from the data cube for 2,920 cm^{-1} (aliphatic CH chains)(g), 1,370–1,540 cm^{-1} from calcium carbonate (h) and 1,581 cm^{-1} (i) from a

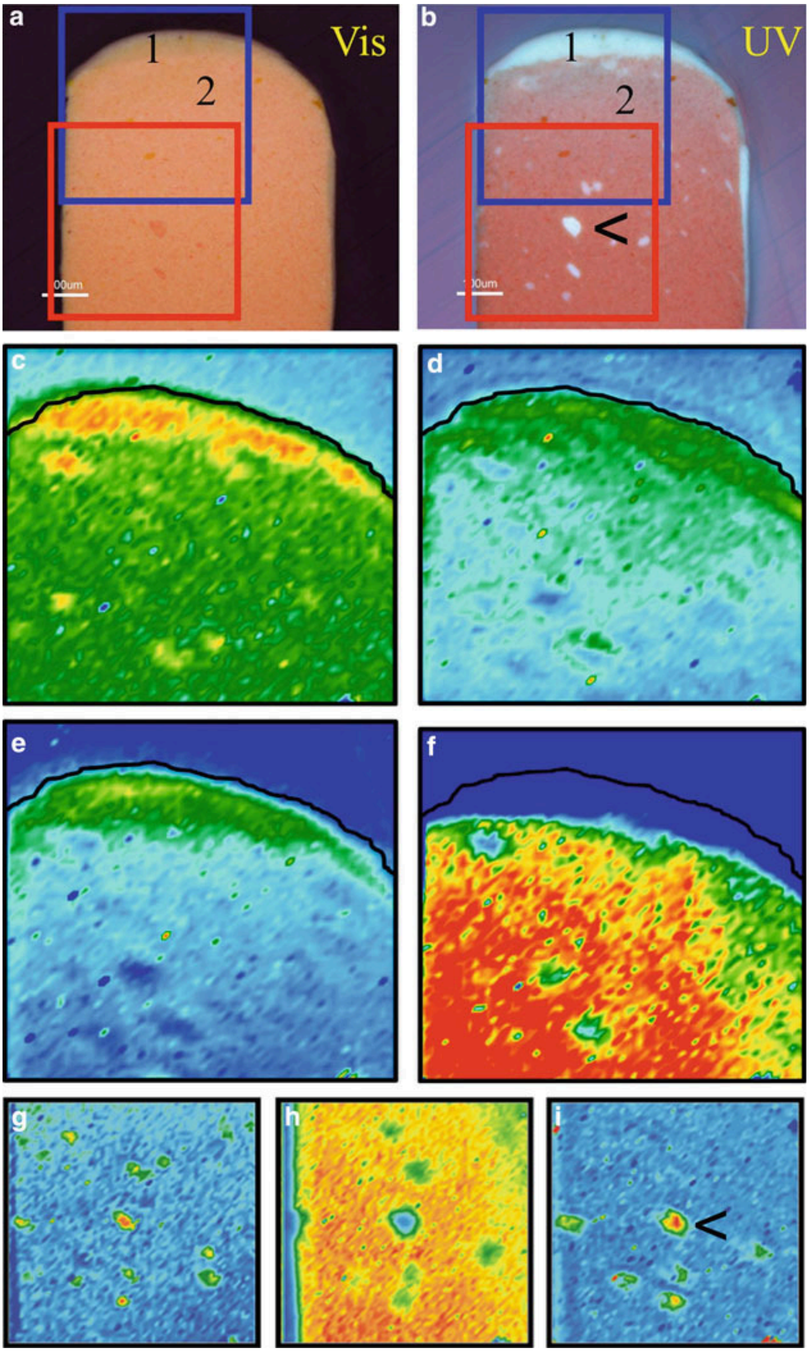

Fig. 4 Light microscopy (**a**: VIS en **b**: UV-fluoresence) and imaging FTIR maps (**c**–**i**) of an Argon ion polished section of van Hemert's paint with exuding material on top. The maps (**c**)–(**i**) correspond to specific wavelength discussed in the text; the red and blue squares to maps (**c**, **d**, **e** & **f**) and (**g**, **h** & **i**) respectively

high intensity peak in aluminium stearate (Al-soap),[1] which is a dispersion and gel-forming agent used in oil paints (Tumosa 2001; Mayer 1991). The FTIR spectrum of the fluorescent spot (arrow) shows a high relative concentration of FTIR features of Al-soaps as well as those from esters.

These results point to a conclusion that the fluidised surface paint contains less solid materials and Al-soaps relative to the main paint mass. Fluorescent vesicles in the bulk of the paint contain Al-soaps and ester bonded oil derived components. Al-soaps were confirmed by Magic Angle spinning solid state NMR but compared to an intact Al-soap reference, the soaps in the paint and the tube are degraded and point to acyl-hydroxy-Al-soap with probably just one fatty acid chain attached (van Eck 2008). The difference between the bulk paint and the more fluid surface paint was further studied with electrospray mass spectrometry (ESIMS) and direct probe temperature resolved mass spectrometry (DTMS).

Identification of the Organic Constituents by Mass Spectrometry

Comparative studies by DTMS and GCMS were performed on the different paints sampled from the selected painting from 1992 (see Fig. 1c), the Fleischfarbe paint tube itself and the tube paint drawdowns after 7 years of drying. Analyses of drips from the drawdowns after seven or more years were limited to studies by DTMS.

The GCMS methodology developed by Van den Berg et al. (2001) was used to quantify biological ester bound and free i.e. non-ester bound fatty acids and diacids as ethylester and silylether derivatives. Figure 5a shows the distribution of the palmitic, stearic, oleic and azelaic acid in the paints indicated in Fig. 1c, the tube paint and the predrip-stage drawdowns (Dd A and B) from 2005 shown in Fig. 2b. Ethyl and silylether derivatives are summed in Fig. 5a. The linolenic and linolenic acid content of the tube paint (about 65 %) is not included in the graph.

All painting samples include azelaic acid (black) as main constituent with lower amounts of palmitic (blue), stearic acid (green) and only a few % of oleic acid (dark pink) that was still present in the drawdowns made in 2005. The reference paints 1 and 2 have lower relative amounts of azelaic acid and still remaining oleic acid (with a much higher % in the alizarin paint 2) even after about 12 years of drying. These results demonstrate that chemical drying had taken place completely. The surprisingly high relative amounts of azelaic acid are possibly due to an unknown added drying catalyst. Only painting sample 3 showed a significantly different ratio of stearic acid to palmitic acid, pointing to the possibility that stearic acid moieties are preferentially retained. In this instance the position of sample 3 at the top of the

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[1] Aluminium stearates consist of a technical mixture of soaps with predominantly stearic acid moieties. They will be referred to as Al-soaps.

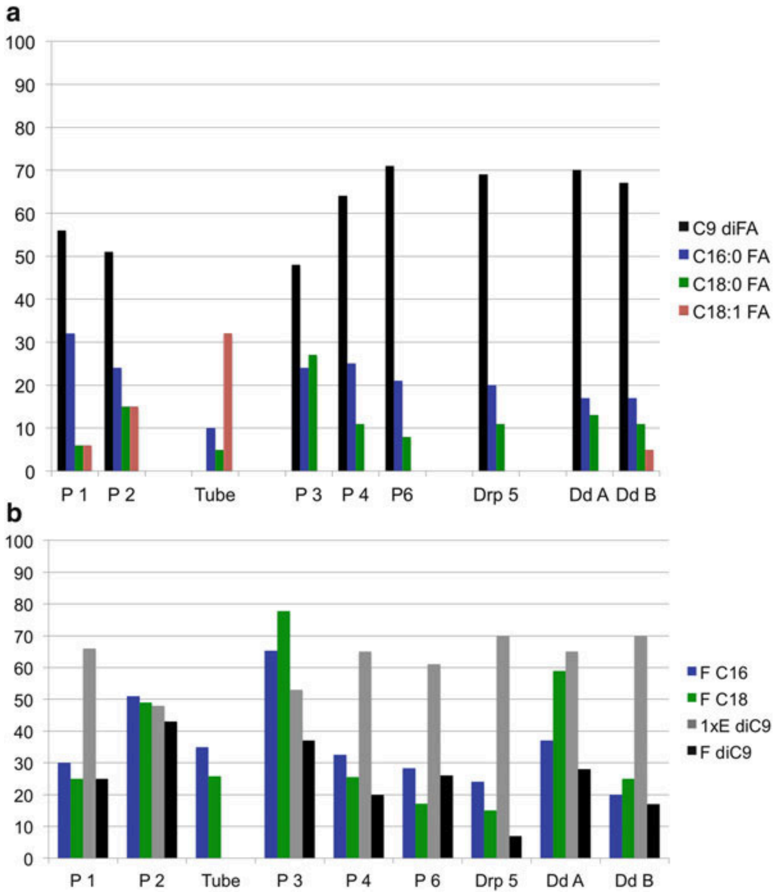

Fig. 5 Graph (**a**) shows distribution of fatty acids (*FA*) and azelaic acid (*diFAC9*) released from paint using the derivatisation methodology of Van den Berg et al. (2001). The numbers correspond to paint sample positions shown in Fig. 1(**c**) indicating Paint (*P*), drip (*Drp*), drawdown thin paint 2005 (Dd **a**), drawdown thin paint 2005 (**b**) and the pink Norma tube paint (Tube). Graph (**b**) shows the distribution of the % non-esterified acid groups as fatty acids and diacids in the samples. The 1xE diC9 is azelaic acid attached to the glycerol moiety while F diC9 is free azelaic acid

swatch probably leads to a preferential loss of fluid exudate due to gravity while Al-stearates remains.

Figure 5b shows the percentage of free (F) i.e. non ester-bound or ionically bound fatty acid moieties as silylethers. The fatty acids in the tube paint are mainly esterified as acylglycerol compounds. The free palmitic and stearic acids are present as metal soap or ionically attached to calcite as suggested by the 13C NMR data (van Eck and Blaakmeer 2011). The C9-diacid with one acid group at the △C9 position free and one group still ester bound is a main constituent in all paint samples. “Free” diacid amounts are relatively high in the alizarin paint P2, the pink paint P3 and the

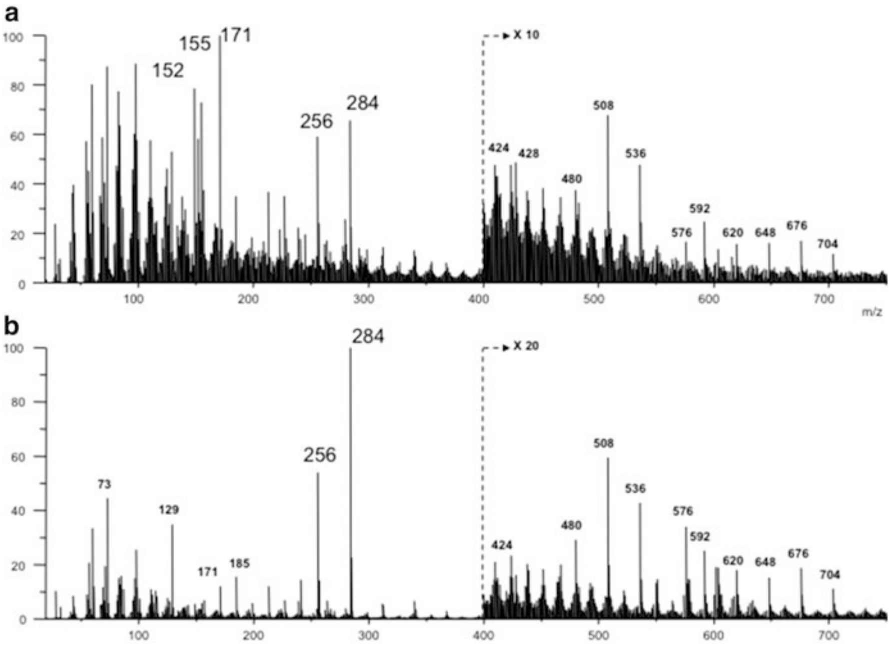

Fig. 6 Direct temperature mass spectrometric summary spectra (*DTMS*) of the fluidised surface paint (**a**) and the underlying rubbery bulk paint (**b**) from the *Seven* series 1992 painting

thin drawdown A. The palmitic and stearic acids are in high concentration in P3 in a free or ionically bound state as metal soap or bound to mineral surfaces. Although the relative amount of azelaic acid is high in the drip material 5, most of that azelaic acid is present in azelaic mono-glycerolester form. Drip 5 had a low % of free azelaic acid (<10 %) whereas paint 3 has a percentage of 35 % free azelaic acid.

Since FTIR microscopy showed a difference between the more fluid paint at the top and the more rubbery bulk paint below, separate sample was obtained from these layers for DTMS and ESIMS analysis. Figure 6a, b shows the DTMS spectra of the surface paint and the underlying bulk paint respectively. These spectra are summation spectra over the mass range before the appearance of cross-linked fractions at higher temperature (beyond scan 60). The lower bulk paint shows high intensity peaks for palmitic (m/z 256) and stearic acid (m/z 284). Stearic acid has a higher intensity than palmitic acid which could correspond to an addition of Al-stearate, a common additive in tube paints and shown to be present by FTIR microscopy. Peaks at m/z 550, 576 and 604–606 correspond to acylglycerolester compounds with combinations of palmitic and stearic acid. In addition we observe peaks at m/z 592, 620, 648, 672 and 704 from beeswax a common suspension agent in tube oil paints (Mayer 1991; Izzo 2011). A main difference between the bulk paint and the more fluid surface paint is the presence of high intensity peaks for C9-diacid (azelaic acid) at m/z 152 and 98, and peaks at m/z 155 and 171 that point to mid-chain-O-functionalised fatty acids like 9,10-epoxy-stearic acid and related keto- or hydroxyl-compounds that lead to a m/z 155 EI fragment ion (Van den Berg 2002). The stearic acid relative intensity is much lower in the surface paint. The intensity of m/z 280 interpreted as a [M-H2O] ion from a keto-stearic acid is relatively high. The combination of higher m/z 280, 155 and 152 is also seen in medium exudate forming from paints by Riopelle (Bronken and Boon 2014), and from black paint in the painting from 1960 by Soulages (Boon, unpublished results). Similar features were observed in the drip that developed from the impasto drawdown material (Fig. 2c) that was sampled in 2010 and later in 2012.

DTMS of the pink Norma Fleischfarbe nr 213 paint showed features of triglycerides with fragment ions of di- and monoacylglycerols and acyl moiety ions at m/z 256, 260, 262, 264 and 284 from palmitic, linolenic, linoleic, oleic and stearic acid (Boon et al. 2010). A small amount of beeswax was also found with peaks at m/z 592, 620, 648, 676, 704 from palmitoyl waxesters with alcohol chain length from C24 to C32. Positive ESIMS of a chloroform-methanol extract (3/1) of the tube paint shows high peaks for triglyceride C55:4 (m/z 873), C55:3 (m/z 875), C57:5 (m/z 897) and C57:6 (m/z 899). The composition of the basic hydrolysates of the extracts analysed by GCMS and ESIMS was 8.2 % palmitic acid, 4.3 % stearic acid, 19.7 % oleic acid, 62.2 % linoleic acid and 5.6 % linolenic acid. So the main triglycerides in the tube paint identified are [3x C18:2 FA] and [C18:1, C18:2 and C18:3 FA] with m/z 897, and [C18:1, C18:1, C18:3 FA] and [C18:1, C18:2, C18:2 FA] with m/z 899. No azelaic acid was found which points to an excellent preservation of the paint in the tube. This distribution is very different from linseed oil with the main triglyceride [C18:3, C18:3, C18:3 FA] at m/z 890 (Van den Berg 2002). The drying index (DI) for the tube paint could be calculated using the relative amounts of fatty acids obtained by GCMS. The value of 72 for the tube paint is rather close to the critical value of 70 when an oil paint will never dry (Mayer 1991). For comparison, a DI for linseed oil would be 140 and for sunflower oil 71 when analysed under the same conditions as the tube paint.

The low DI and the absence of azelaic acid and other diacids suggests that the paint must have been made with a minor amount of a high linolenic moieties containing drying oil. During the ICOP symposium it became known that the paint was made almost completely with semi-drying oil like sunflower oil.[2]

The distribution of fatty acid moieties between surface and lower bulk paint was further investigated in extracts after basic hydrolysis and chemical work-up using negative ion nanospray-ESIMS shown in Fig. 7. Figure 7a shows high intensity peaks for C9-diacid at m/z 187 and relatively low peaks for palmitic (m/z 255) and stearic acid (m/z 283) [all M-H negative ions]. Several oxygen functional stearic acids are observed in the fluid surface layer with one (m/z 297), two (m/z 315), three (m/z 329) or four (m/z 331) oxygen insertions in the fatty acid chain. These peaks were identified on the basis of their exact mass. The hydrolysate ESIMS in Fig. 7b of a sample taken from the bulk of the paint mass illustrates that the ratio of C9-diacid

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[2] The use of sunflower oil in this paint has been confirmed by a representative of Schmincke (Dr W. Mueller) during the ICOP 2013 conference. The composition of the paint has been revealed to Schulz and coworkers since then. See Franken et al., Chap. 22, p. 333.

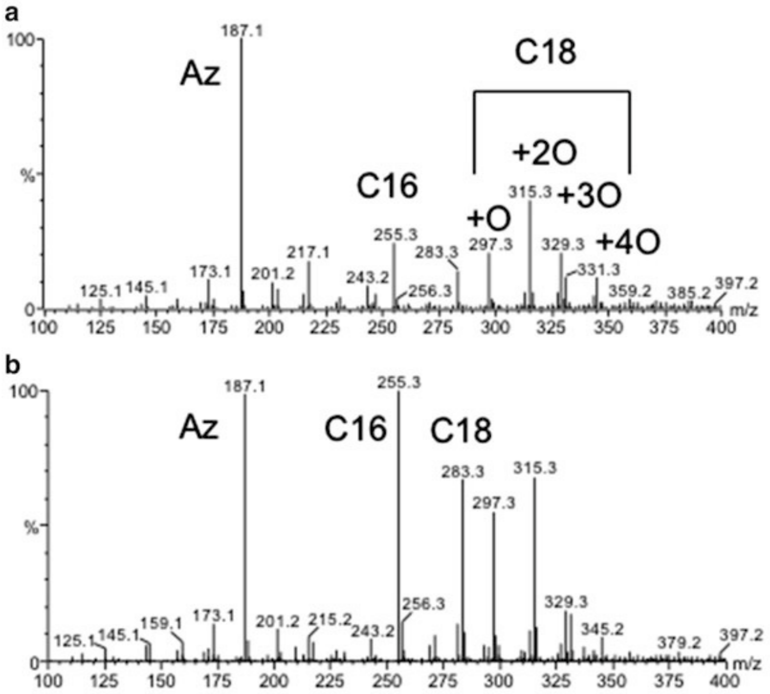

Fig. 7 Negative ion electrospray mass spectrometry (*ESIMS*) of basic hydrolysates of the fluidised surface paint (**a**) and the underlying rubbery paint (**b**)

to palmitic and stearic acid is quite different. Some oxygen-functionalised stearic acids are also relatively higher than the C9 diacid. Examination of the negative ion ESIMS of the ethanol extracts of these paint shows similar patterns but with intact acylglycerides with C8- and C9-diacids, and glycerides with palmitic, stearic and O-stearic acyl moieties (Boon et al. 2007, 2010). The free palmitic and stearic acids are very prominent deeper in the paint where the stearic acid to palmitic acid ratio is >2. In conclusion, the bulk of the paint contains more apolar fatty acid containing compounds while the more fluid surface material primarily contains acyl-glycerol moieties with more polar diacid and O-C18 fatty acid compounds attached.

Discussion

Oil paint, a mixture of drying highly polyunsaturated vegetable oils and inorganic materials, develops into remarkably stable durable material that lasts for many centuries on easel paintings. The chemically drying organic materials play a decisive role in the stabilisation to a dried substance. While there is now a body of evidence for the formation of radicals, reaction with oxygen and formation of cross-links in drying oils (Van den Berg 2002), the molecular level interaction of mineral components in paint including pigment and extenders with the organic materials is less well understood. Drying oils without mineral additions can develop into a viscous mass upon atmospheric exposure so a dried paint could be visualised as a viscous mass that encapsulates the particulate mineral matter. Although this may be true for relatively fresh oil paints, exposure over centuries to atmospheric carbon dioxide and water has an impact on the stability of the biological ester bonds of the original triglycerides. Boon et al. (1997) showed that a large proportion of the acylglycerols in century-old dried oil paint was hydrolysed. The de-esterification over time was further confirmed by Jorrit van den Berg with a specific chemical work-up method combined with GCMS (Van den Berg et al. 1999, 2001). Similar results have been published by Schilling et al. (2007). Hydrolysis of biological ester bonds can completely dissolve the cross-linked oil network, thus presenting a challenge for understanding the preservation of aged oil paintings. Boon et al. proposed in 1997 that the acid groups of the organic matter in aging oil paint play a vital role in stabilisation of the oil paint over time. The relatively large amount of diacids that form by oxidation of the △-C9 double bonds can form very stable structures in three dimensions (Boon 2006). Indeed metal soap structures of azelaic acid are remarkably heat stable to nearly 300 °C (Ibidapo 1996). Another factor of importance influencing the stability of oil paints is the interaction of the acid groups in the oil network with surfaces of pigments and extenders. This is particularly important in the early stages of drying when the △-C9 double bonds of unsaturated C18 fatty acids turn into diacids with one side attached to the biological ester groups of the triglyceride moieties (Verhoeven et al. 2006). The molecular level interaction of oil derived materials and mineral surfaces has not been investigated for oil paints. Osman and Suter (2002) investigated the interaction of saturated and unsaturated fatty acids with clean calcium carbonate surfaces on a molecular level in the context of the role of fatty acyl derivatised calcium carbonates for ore flotation separation. Important for oil paint studies is their observation that unsaturated fatty acids in interaction with the mineral surface can develop cross-links. Applying this observation to a model for drying oil and calcium carbonate as mineral surface, we postulate that oxidizing polyunsaturated triglycerides will attach via ionic bonds to the mineral surface but will also react with each other via radical cross-linking processes. This ensures a good anchoring of the binding medium components to the available mineral surfaces in the paint. However, the surfaces of calcium carbonate extenders are not always clean and often treated with surface modifiers to increase wettability and flow (Gysau 2006) so interaction to and stabilisation of an extender surface can be inhibited. Oil paint contains many different pigment mineral additions, so a variety of different behaviors are expected and have indeed observed in the organic composition of young ageing oil paints (Keune et al. 2008). Oil paint making is not just mixing drying oil and pigment solids. The Artist's Assistant by Carlyle (2001) gives insight into the paint maker's kitchen and early paint industry in the nineteenth century. In the course of the twentieth century the scale of the paint making process increases significantly and recipes for manufacture remain secret. This factor and that the fact many of the archives of colourmen and small paint industries are lost presents a paucity of historical information about how oil paints were prepared. The archives of Winsor & Newton dating from 1847 onwards have been saved in recent years and made partly available to the public (Carlyle et al. 2011). These records show the increased complexity of paint formulations from the nineteenth century onwards, while simpler mixtures of oil and pigment may have been used in the workshops of the early oil painters. One important surfacing fact is that nondrying oils are mixed with drying oils. Furthermore, tube paints require stabilisation. Mayer (1991, 184–187) discusses several strategies used to stabilise tube oil paints. Addition of waxes and metal soaps leads to buttery paints when used in small amounts. Mayer warns about the percentage by weight and by volume mostly in connection with tinting strength, but light weight solids in the paint can lead to relatively large amounts of Al-stearate for example if measured by volume. Al-soaps are mixed into the dry solids first to increase wettability and to ease oil absorption, which implies that the industry modifies the surface quality of the dry solids in paints. Corkery (1998) mentions that Al-tri-fatty acids are expensive, difficult to make and hard to keep stable. The quality of Al-soaps varies considerably and technical grade may contain a large percentage of free fatty acids (Tumosa 2001). This implies unfortunately that free acids in technical grade Al-soaps will react with surfaces just like the free fatty acids in the experiments of Osman and Suter (2002). So although ideally, high quality artist grade oil tube paint should consist of oil and pigment, in practice the cheaper grades of paint contain extenders and gel-forming agents such as Al-soaps up to high percentages. One may expect therefore that these cheaper formulations can behave in unexpected and different ways.

The analytical data on the Norma Fleischfarbe points to an oil with very small amounts of linolenic acids and large relative amounts of linoleic and oleic acid. The drying index is so close to the critical value that formation of a strong viscous network of linolenic and linoleic fatty acid moieties is nearly impossible. The linolenic and linoleic acyl moieties react relatively rapidly compared to oleic acid moieties that do not contribute to cross-linking but rather act as end-cappers limiting the size of the cross-linking material. Initially good quality Al-soaps should still have stabilised gel formation as the paint was buttery but with advancing degrees of oxidation of the unsaturation and the formation of increasing relative amounts of polar groups, this gel-state is likely to have become compromised. Since almost no unsaturation is present after about 10 years of drying of the softening paints of the painting, it is clear that appearance of fluid exudate is not due to non-dried triglycerides or original oil fractions. Even after a few years of drying, samples from the drawdowns contained hardly any unsaturated fatty acids and the relative amount of azelaic acid moieties is high. The separation of fluid fractions from the bulk of the paint is therefore due to a physical separation between developing polar fractions, the absence of anchor points for acid groups on surfaces and the presence of apolar fractions inside the paint. The relative amount of acid groups generated from the unsaturated fatty acids is very high, which would require a large reservoir of acid neutralizing materials in the paint formulation to compensate for this rapid increase in acidity. Calcium carbonate in the paint could in principle play this role but all calcium containing material in the paint is sequestered in aggregates as SEM at high magnification has demonstrated. Osman and Suter (2002) have shown that fatty acids can attach to clean calcium carbonate surfaces. Such attachment may either have happened in the production phase of the paint or at a later stage when the acidity developed upon oxidation. One factor of importance resulting from the ^{27}Al-NMR studies (Van Eck 2008) is that the Al-soaps utilised were already degraded in the tube paint to hydroxyl-aluminates with one fatty acyl group attached, which implies that there must have a been a large percentage of free stearic acids present in the metal soap added to the pigment and extender solids. Addition of free fatty acids in the degraded Al-soap must have covered a large percentage of the available surface area of the calcium carbonate filler. Apart from the degraded Al-soap, mass spectrometry also discovered beeswax esters that play a role as wettability agents (Mayer 1991) but these also added more apolarity to the paint before any mixing in of the oil. The fluid exudate at the surface and in the drips is more polar than the remaining paint substance underneath the fluidised surface. A lot of that polarity is in the form of acylglycerides with ester bonded azelaic aids and midchain oxidised stearic acids. These compounds are physically separated from the more solid paint mass that shows vesicles of fatty substances clearly excluded from the paint mass. The results of the present study further suggest that these vesicles are remnants of the fluid exudate. Vesicles and surface exudate show the same fluorescence and are therefore a good tracer of physically separating fractions. Similar fluorescence has also been observed on the surface of a painting by Riopelle and in cross sections of its exuding paints (Bronken and Boon 2014). The fluorescence of the exudate from the 7-year dried fluidizing Norma Fleischfarbe is not caused by one compound but is a property of substances that form unusually broad peaks upon HPLC analysis (Van Bommel, 2013, personal communication), which suggest that the fluorophores are attached or part of oligomeric fractions. The distribution of remaining fluorescent vesicles in the paint with FTIR features pointing to Al-soaps suggests that the Al soaps are not well dispersed in the paint initially or have aggregated into these vesicles. The presence of esters in these vesicles furthermore suggests that materials with the original biological ester bonds have accumulated there. This supports the idea that polar fractions develop inside the body of the paint as vesicles that fuse together and find their way to the surface given sufficient time. It is remarkable in this respect that exudates take about the same time of 6–7 years for appearance for paints from Schmincke (van Hemert) and paints from other manufacturers used by Walls and Meese.

The mechanism is complex and probably not related to one factor. The semidrying oils in the paints form many oligomeric polar fractions that should be stabilised by acid neutralizing surfaces in the paint solids. The Al-soaps degraded possibly due to exposure to moisture before use which consequently added free acids and Al-acyl-hydroxides to the solid matter. Beeswax added further apolarity to the surfaces but beeswax is often used without much of a problem. Then oils are mixed into this paint formulation and tubes are filled. Upon use as paint, oxidative cross-linking begins forming a viscous substance that encapsulates the solids first but fail to create molecular bridges sufficiently to stabilise the paint mass. Al-ions from degraded

Al-soaps might drive the oxidation further since they can act as secondary drier (Mecklenburg et al. 2013). The polar Al-OH-soaps appear to function as nuclei for other polar substances in the drying oil paint leading to polar micelles where apolar ester bonded acylglycerides form the core and acid groups from azelaic esters and hydroxyl group from Al-hydroxides are concentrated at the surface. The calcium carbonates in the paints are aggregated and are likely unable to stabilise the ever increasing relative amounts of acidic fractions as oxidation of the semidrying oil progresses. First, thin films of exudate develop at the surface followed by collapse of sharp impasto features where the paint looses consistency. Thicker paints incorporate a larger reservoir of exudate that is physically separated and flows out under the force of gravity. Moisture that could fluidise the polar micelles in the paint facilitates the exudation process. The remaining paint has lost quite some medium and begins to show a rubbery appearance. It is remarkable that this paint is completely soluble in acetone unlike the two “hard” paints from Lefranc-Bourgois.

Van Hemert never stopped using Schmincke paint since he liked their colour and consistency. None of these paint had any drying problems after a long period of time. The behaviour of the pink Norma paint from the period 1990–1995 suggests that there has been a formulation fault due to failing ingredients. Its formulation (ingredients, mixing procedure etc.) was an industrial Schmincke secret. There is some evidence in messages on the Internet about sticky Fleischfarbe Schmincke paint (Petronella 2004) pointing out that van Hemert was not the only one that suffered from a faulty paint. In this message Petronella reports that her pink paint began to flow after about 10 years.

Although there are now many more cases of sticky and dripping paints not all the cases may have the same causal factors, and the unique circumstances of each needs to be considered. In some cases the oil itself may be an issue, in other cases faulty additive(s) may play a role, a lack or a covering of anchor points for acid fractions in the paint is potentially another factor. However, this study suggests that the increase in polarity in relation to failure to anchor these polar fractions inside the paint is the main physical cause of the formation of exudates that create sticky films or even drips depending on the size of the polar fluid-producing reservoir.

Conservators are now wondering how to stop the process. Theoretically an addition of anchor points by addition of metal ions would be a way to bind the acidic fractions. This approach is presently tested on samples from a painting by Riopelle (Bronken, 2013, personal communication). Even exposure to ionizing radiation thus renewing the radical chemistry in the paint has been tried with some success (Schultz 2011). These approaches may work despite considerable experimental difficulties. There is however a caveat: when exudates appear after so many years, the structure of the paint itself has changed too. The distribution of fluorescent polar vesicles inside the pink Norma paint can be seen as evidence for a severe disturbance of the paint consistency. In our study it was noted that the speed of flow was related to moisture suggesting that atmospheric water facilitates the exudation of polar fractions. Drying the dripping painting at 80 °C for several hours indeed stopped dripping in the case of the painting by Piene (Schultz 2011), but it is not clear whether this will remain a permanent change in the paint. One suggestion for treatment could be to keep the painting on a flat surface and develop a treatment to diminish the exudates from the reverse, but this may not always be a practical option. Artists like van Hemert and Walls, and owners of their paintings however consider their works ruined due to loss of intent caused by changes in the surface appearance of the paint.

Appendix

Experimental Details

Microscopy

Light microscopic images (VIS and UV-fluorescent) were obtained with a Leica DMRX microscope (Leica, Wetzlar, Germany). The Bio-Rad Stingray (Bio-Rad, Cambridge, MA), combining the Bio-Rad FTS-6000 spectrometer equipped with a Bio-Rad UMA 500 infrared microscope with a 64 × 64 mercury-cadmium telluride (MCT) focal plane array camera was used to record the FT-IR images (see van der Weerd et al. 2005). A Philips-FEI XL-30 FSEM coupled to an EDAX energy dispersive analyser was used for SEM-EDX. The ion polished section (Boon et al. 2008) was covered with a few nm of gold in vacuo using a sputter coating system.

Mass Spectrometry

A JEOL SX102-102A mass spectrometer was used for DTMS (Direct Temperature resolved Mass Spectrometry) equipped with a Pt/Rh (9/1) filament (diam.100 μm) probe for in-source MS. Spectra were obtained at 16 eV electron ionisation over a mass range of 1,000 Da at a cycle time of 1 s and acceleration voltage of 8 kV (Boon 1992). Degree of esterification was determined by GCMS after derivatisation of paint samples using the method of Van den Berg et al. (2001). Tube paint was extracted with chloroform/methanol (3/1). Part of the extract was analysed directly with ESIMS. Another part subjected to basic hydrolysis, worked up and analysed by ESIMS or by GCMS after silylation. Paint samples were also weighed (400–600 microg) into 1 mL tapered vials. For ethanol extraction 100 microL ethanol was added with tridecanoic and tetradecanedioic acids as internal standards. The samples were extracted for 18 h under ambient conditions. Extract were analysed directly with ESIMS. Hydrolysis of ethanol extracts: a 0.1 M ethanolic NaOH solution with tridecanoic and tetradecanedioic acids as internal standards was added to the samples. The hydrolysis took place in an oven held at about 80 °C for 1.5 h. Each solution was shaken and centrifuged after extraction or hydrolysis. The extract or hydrolysate was subsequently transferred to a vial containing cation exchange resin (DOWEX HCR-W2 ion-exchange resin, Sigma–Aldrich) and left for 30 min to remove pigment-derived cations. The supernatant solution was removed from the resin and transferred to a new vial. For all ESIMS, Ethanolic ammonium acetate was added until a final concentration of 10 mM ammonium acetate was achieved.

Nano-ESI–QTOF–MS was performed on a Q-ToF2 instrument (Micromass Limited, Wythenshawe, UK). The solutions were sprayed with Econo10 needles or BG-10-58-2-CE-20 needles (New Objective, Woburn, USA) with a flow of approximately 10–80 nl/min. Data were processed using the MassLynx V3.5 software (Micro- mass Limited, Wythenshawe, UK). Mass spectrometer conditions: capillary voltage: 2 kV, cone voltage: 10 V, collision energy: 10 eV, TOF: 9.1 kV and the detector was set at 2,150 V in the positive mode and 2,300 V in the negative mode.

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