

Klaas Jan van den Berg · Aviva Burnstock · Matthijs de Keijzer · Jay Krueger
Tom Learner · Alberto de Tagle · Gunnar Heydenreich *Editors*

Issues in Contemporary Oil Paint

This volume represents 27 peer-reviewed papers presented at the ICOP 2013 symposium which will help conservators and curators recognise problems and interpret visual changes on paintings, which in turn give a more solid basis for decisions on the treatment of these paintings. The subject matter ranges from developments of paint technology, working methods of individual artists, through characterisation of paints and paint surfaces, paint degradation vs. long time stability, to observations of issues in collections, cleaning and other treatment issues as well as new conservation approaches.

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Foreword

It is a great pleasure to present the Proceedings of the Issues in Contemporary Oil Paint (ICOP) Symposium that was held in 28–29 March, 2013, in Amersfoort at the headquarters of the Cultural Heritage Agency of the Netherlands, RCE.

Our Agency is at the heart of cultural heritage in the Netherlands. Our research group is concerned with the evaluation and preservation of our heritage in the broadest sense and the research directions we need to follow in order to guarantee a sustainable heritage. Along with national and international research partners at museums, universities and archives, we conduct research, characterise materials and analyse change processes. The Agency ensures that third parties can apply the knowledge that we can provide.

The ICOP symposium was the first symposium focused on modern paints since the Modern Paints Uncovered (MPU) conference held at Tate in 2005. Whereas MPU mainly presented research on modern synthetic paints especially on acrylics, ICOP chose to focus on modern oil paints entirely. Many modern artists continue to work with oil paints, and modern oil paints increasingly become a challenge for conservators and collection keepers. Therefore it was felt by the organisers that it was time to organise a meeting which could discuss these challenges by presenting information on historical and artistic production, scientific research on degradation phenomena, and developing alternative conservation approaches.

ICOP marked the end of a 4-year Research Agenda, for our Agency.¹ In one of the programmes in the Research Agenda, *Object in Context*, the RCE research group generated knowledge on the production of and changes in heritage objects in their artistic, cultural and social contexts. Under the leadership of Klaas Jan van den Berg, the '20th century oil paint project' contributed to the outcome of the Agenda. The project brought many institutions together and was a breeding ground for

¹Outcomes of this Research Agenda are accessible on-line: <http://www.kennisvoorcollecties.nl/en/researchagenda/>.

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Set Back the Race: Treatment Strategies for Running Oil Paint

Verena Franken, Gunnar Heydenreich, Elisabeth Jägers, Wolfgang Müller, Jenny Schulz, and Stefan Zumbühl

Abstract This study examines the phenomenon of semi-drying oil paint and liquefaction processes in contemporary oil painting. It aims to achieve a deeper understanding of the complex processes and to evaluate new treatment strategies for the subsequent curing of liquefied paint. Instrumental analysis of liquefied paint samples reveals that all samples contained predominantly semi-drying sunflower and/or safflower oil that have major impact on the liquefaction process. In thick paint layers low molecular weight polar fractions are created by decomposition of triglycerides that are mobile within the paint layer. Hardening of liquefied oil paint samples can be achieved by heating them to between 70 and 80 °C. The degree of hardness is dependent on the temperature, the length of exposure and the film thickness. A significant loss in weight suggests that low molecular weight components evaporate and that the hardening is primarily a physical process.

Keywords Sunflower oil • Safflower oil • Buff Titanium • Meese • Drying defects • Liquefaction • Heat treatment

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Introduction

Non-drying oil paint is a phenomenon in contemporary art and paintings made using these materials may present challenging conservation problems. Case studies suggest that the dripping occurs often after about 5–7 years, in particular where the paint is thickly applied. The phenomenon occurs in paints from various manufacturers. Previous research has shown that the tacky and visco-elastic liquid paint occurs in superficial layers whereas deeper layers appear more stable (Pfandlbauer 1993; Schulz 2008). The affected paint layers are soft and tacky, and where thickly applied, a secretion of binding medium can occasionally be detected, and in an advanced phase the oil paint is viscose and may form drips. The aged and liquefied paint is unsightly and often requires treatment. It was also established that the phenomenon of liquefaction may stop once all the volatile components have leaked out. Case studies that exhibit dripping paint include paintings by Jonathan Meese, such as *Der Kotbart erwacht* (2001/2002) (Schulz 2008), *Portrait VII* (2003) and *Kleiner Hund* (2005) (Fig. 1).



Fig. 1 Jonathan Meese, *Kleiner Hund*, 2005, Contemporary Fine Arts Berlin, detail with paint drips

Background and Current State of Research

The chemical alteration of oil paint has been investigated by a number of researchers (Boon and Ferreira 2006; Kamal-Eldin 2003; Van den Berg 2002; Mallégo et al. 2000; Frankel 1998; Chan 1987; Richardson and Korycka-Dahl 1984). Explanations for the cause of dripping paint suggest a physical rather than chemical liquefaction process dependant on rheological properties of the paint, together with the accumulation of low molecular weight species and unbound polar components within the paint caused by hydrolysis and oxidation (Götz 2003; Hoogland et al. 2007; Schulz 2011). The acidic products may be mobile within the film and influence on the liquefaction state.

Linseed, Poppy-Seed, Sunflower and Safflower Oil

To date linseed oil is the principal binding medium for oil paints and previous investigations on drying properties and drying problems have concentrated primarily on linseed oil. However, as paints containing linseed oil tend to yellow with age paint manufacturers also added other semi-drying oils like poppy-seed oil, particularly for white and blue paints.¹ In more recent decades poppy-seed oil was commonly replaced by semi-drying oils like safflower or sunflower oil. Sunflower oil and safflower oil exhibit different drying properties to linseed oil due to a relatively low content of poly-unsaturated fatty acids.² As a result, they form a less cross-linked insoluble network structure, which is weakly bonded. Preliminary studies showed that oil paints based on semi-drying oils achieve only a moderately stable paint matrix (Eibner 1922, pp. 186, 269). Following these early fundamental studies, it is possible to postulate that various processes may contribute to the liquefaction of oil paint. Paint composed of a high proportion of sunflower and other semi-drying oils may be one factor. Another factor may be the formation of mobile and volatile low molecular compounds as decomposition products from triglycerides in oil paints (cf. Zumbühl et al. 2014a). The mobile fractions may destabilise the paint matrix whereby a flowing phase can occur in the surface film. Drying of oil paint may be inhibited by the presence of selected pigments, fillers and organic additives such as aluminium and zinc stearate, clove oil or beeswax (Izzo 2011, p. 143). However, test films of pure sunflower and safflower oil have been observed to liquefy after 5–7 years and formed drips, suggesting that the process can occur in non drying oils alone.

¹Related drying defects have been reported (Eibner 1930).

²Sunflower oil has a fatty acid composition of (by weight) 7 % C16:0 (palmitic acid), 5 % C18:0 (stearic acid), 23 % 18:1 cis-9 (oleic acid) and 65 % C18:2 (linoleic acid) (Schilling et al. 2007, p. 130).

Past Treatment of Affected Paintings

The increasing number of paintings affected by delayed dripping is of concern to artists, art collectors, paint manufacturers and conservators. There are so far no well-established methods for the treatment of paintings that exhibit liquefaction defects. Reworking of the painting by the artist or the application of a protective coating has caused ethical controversies (Althöfer 1980, p. 18). One approach has been to remove the drips and to rebuilt sunken impasto (Schulz 2008, p. 84). More recently conservators have attempted to search for possible means of stabilizing the paint and preventive treatment. Attempts were made to stabilise the softened paint by the injection of charged metal particles or to harden it with gamma rays (Schulz 2008, 2011). Whilst the first method appeared to be unsuccessful, the exposure to high energy radiation stabilised the paint. However it remains a theoretical approach as it is impossible to use this method on paintings for safety reasons.

Objective

The present study aimed to investigate the cause, the process and treatment of the phenomenon in paints containing semi-drying oils in order to expand our understanding of the complex reactions in oil paint. Practical tests explored the possibility of hardening liquefied paint using thermal treatment. Preliminary results suggested that heating changes the consistency of the liquefied oil paints but the mechanism and the potential for application of heat as part of a conservation treatment of a whole painting requires further study. This study aimed to clarify whether the curing attained by heating is primarily a physical process or produces chemical changes in the paint. The question whether a short exposure to high temperatures has the same effect as a longer exposure at a lower temperature was also investigated, together with the long term stability of heat treated paint in relation to fluctuations in relative humidity.

Experimental

Samples, Methodology and Analytical Instrumentation

Sources of sample material were

- Paintings that showed liquefaction defects
- Naturally aged paint samples that partly showed liquefaction defects and
- Fresh paint samples that were produced according to recipes of paints, which generated liquefaction defects in the past (Table 1)

Table 1 Description of the paint samples used for the experimental study

Sample ID	Sample description	Composition	Wet film thickness/ amount	Support	Assigned for
(a)	a1 und a2 Buff Titanium, Daler Rowney®	Sunflower oil, titanium white, Iron-containing pigment, calcium-magnesium carbonate	Small droplet	Object slide	Heat treatment (80 °C, 70 °C, 65, 60 °C, 40 °C)
(b)	b1 Norma® Fleischfarbe Schmincke®	Linseed oil, sunflower oil, titanium white, calcium carbonate, additives	Small droplet	Object slide	Heat treatment (80 and 70 °C)
(b)	b2 Schmincke® rezept 11213	80 % sunflower oil, 20 % linseed oil, safflower oil, calcium carbonate, cadmium pigments, additives	Pastose paint film	Cardboard	Heat treatment
(b)	b3 Schmincke® Rezept 11445	25 % sunflower oil, 75 % linseed oil, safflower oil, calcium sulphate, blue pigments, additives	Pastose paint film	Cardboard	Heat treatment
(c)	c1 Schmincke®, rezept 11213, variation 3	Sunflower oil, cadmium pigments, titanium white, calcium carbonate, additives	2,000 µm, size: ~ 2 x 4 cm	Polycarbonate film	Heat treatment (80 °C, 60 °C, 40 °C), various environmental conditions
(c)	c2 Schmincke®, rezept 11213/Variation 3	Sunflower oil, cadmium pigments, titanium white, calcium carbonate, additives	Max. 7,000 µm	Object slide	Heat treatment (80 °C, 60 °C, 40 °C), various environmental conditions
(c)	c3 Schmincke®	Oil with cobalt siccativ	0,10 g	Object slide	Heat treatment (80 °C, 60 °C, 40 °C), various environmental conditions

Samples (a) were provided by the studio of Jonathan Meese and by the conservation studio Brakebusch.³ The affected paint is Buff Titanium from the series Georgian Oil Colours by Daler Rowney (Table 1). The paint contains mainly sunflower oil as binding medium.⁴ The main pigment is titanium dioxide with traces of iron oxide and calcium-magnesium carbonate. The naturally aged paint samples (b) represent oil colour out of the series Norma[®] by H. Schmincke & Co. (b1). This paint contains linseed oil, sunflower oil, titanium dioxide, calcium carbonate, cadmium pigments and small additives such as beeswax. The samples were manufactured by H. Schmincke & Co. in the 1990s and in 2003 according to recipes from the 1990s. Some samples show liquefaction defects and these represent paint that was used by artists and where drying defects were observed in the past. Additionally, fresh paint samples (c) manufactured according to recipes from the 1990s and pure sunflower oil enabled the impact of external influences on the drying process to be monitored. Within this study we focus primarily on the aged and liquefied paint samples (a, b).

The paint samples were heated at different temperatures and for varying periods in a laboratory oven at 40–80 °C. The samples were exposed to increased temperatures for periods of 24 h up to a maximum of 25 days and examined at intervals of 1 day.⁵ Temperature and humidity were monitored in the oven. With rising temperatures the RH dropped significantly to 3.5–14 %. After treatment sample material was exposed to a relative humidity of c. 45–55 % RH except one sample which was stored at 84 % RH.

All samples were examined by eye with a microscope (10–80× magnification) and mechanically with a needle and a scalpel in order to investigate stages of the drying process, changes of material characteristics and the impact of thermal treatment at different temperatures. Changes of the surface and inner paint bulk morphology were recorded photographically with a digital microscope, VIS and UV-light microscopy. Material properties such as hardness, stickiness and viscosity were evaluated continuously using a thin needle. After testing hardness with a needle and transecting the sample with a scalpel the degree to which the surface and the inner paint had dried could be evaluated.⁶ Samples were

³The paint, which was supplied by the Restaurierungsatelier Brakebusch, was taken from a painting by Jonathan Meese from 2004. The painting was reworked in the artist's studio; the affected paint application was removed and replaced (personal communication, Börries Brakebusch, Düsseldorf).

⁴The P/S ratio is too high for linseed oil. NB: This brand is listed as using 'refined linseed and safflower oil' and 'sunflower oil for the whites' (Pearce 1992). An ESI spectra analysis of the tube colour (bought in 2006) shows a spectra with round about 90 % sunflower oil and no linseed oil (comp. Fig. 6).

⁵Every day one sample was removed from the oven for examination. Removed samples were not returned to the oven.

⁶For testing hardness with a fine needle a pressure of approximately 35 g (measured with analytical balance) was applied. To investigate the inner paint bulk morphology the samples were transected with a scalpel and the paint's cross-section was recorded photographically.

weighed every day with an analytical balance and thermogravimetric analysis was undertaken to qualify evaporating components under isotherm condition at 50 °C over 24 h.

Samples were analysed and examined using a Scanning Electron Microscope with back-scattered electron analysis (SEM-BSE) to localise the accumulations of organic compounds. Gas Chromatography–Mass Spectrometry (GC-MS) was applied to examine the chemical changes in samples (comp. appendix). As GC-MS cannot record all volatile components, as pyrolysis splitting occurs at c. 300 °C and components volatilise too rapidly, nano Electrospray Ionisation Mass Spectroscopy (ESI-MS) was used.

Fourier transform infrared spectroscopy (FTIR) was employed to characterise chemical alteration. Additionally, samples were prepared with a derivatisation technique using sulphur tetrafluoride SF₄ which facilitates the characterisation of functional groups. It helps to distinguish overlapping signals and to characterise acids in the samples (Zumbühl et al. 2011, 2014a). This standardised derivatisation technique facilitates the characterisation of the ageing and degradation conditions of the sample material. It is more specific, because a more precise breakdown in the carbonyl- and carboxyl-bands makes a distinction between ketones and acids possible (Zumbühl et al. 2014b).

Results

The experiments confirmed that heating cured the liquefied sample material in the paint films. The degree of hardness of the paint films was dependent on the temperature in the drying-cabinet, the length of exposure and the film thickness. A complete hardening was achieved at 80 °C after 5–6 days for the Buff Titanium samples (a1 and a2). These samples were soft and tacky before thermal treatment and initially developed a very thin, deformable surface skin before the paint beneath also became more solid (Fig. 2). Hardening of the H. Schmincke & Co. paint samples (Norma[®] Flesh colour) (b1) was achieved at the same temperatures in less time, probably as they exhibited a lower level of liquefaction before treatment.

The tests confirmed that thicker paint layers require a longer period of thermal treatment and apparently a minimum temperature was required to initiate the hardening process. Samples of Buff Titanium heated to 40 °C and 60 °C showed no obvious changes in hardness or viscosity after 6 days (a1 and a2). Even after more than 25 days at 60 °C these samples were soft enough to show plastic deformation, and threads of paint could be pulled from the samples. At 70 °C hardening was achieved after 10 days (Fig. 3). In the course of heating no changes in fluorescence were noticed. During exposure to heat a coalescence of the Buff Titanium sample could be observed, though this also occurred on reference samples at room temperature.

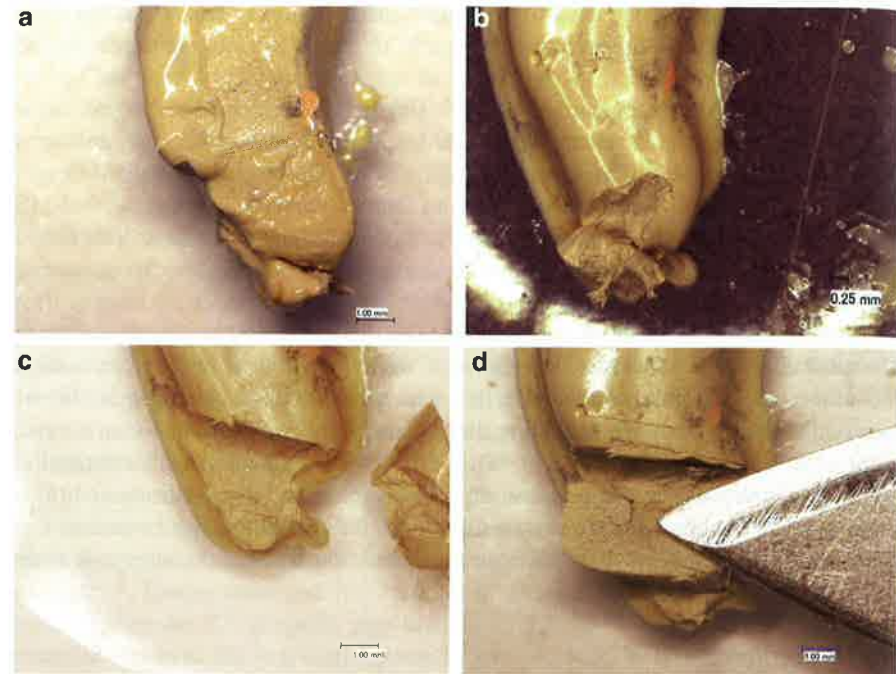


Fig. 2 Buff Titanium samples before (a) and after heat treatment at 80 °C for 2 days (b), 5 days (c) and 6 days (d)

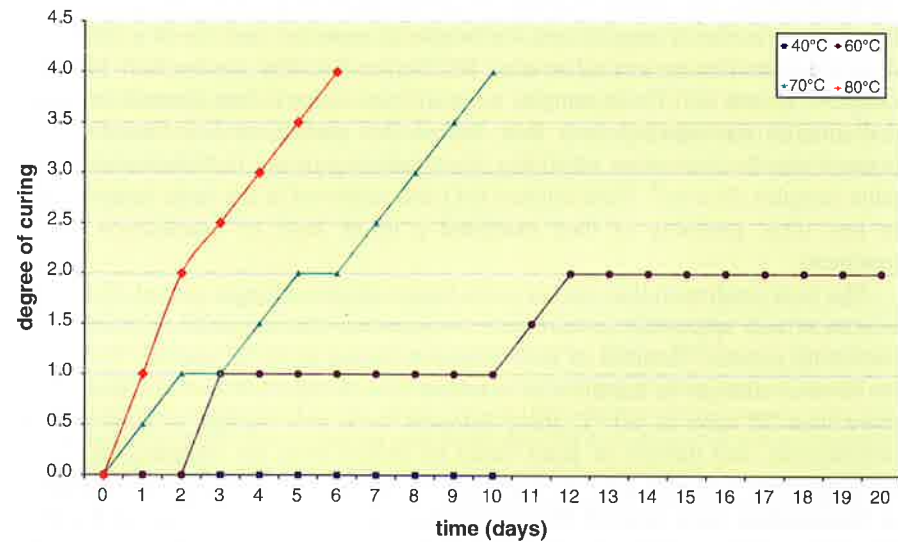


Fig. 3 Degree of curing for Buff Titanium samples after a heat treatment at different degrees (40, 60, 70 and 80 °C)

Thermogravimetric Analysis and Gravimetry

Thermogravimetric measurements showed that the hardening was accompanied by a considerable loss in weight. This also occurred in samples heated to below 50 °C. The loss in mass of the pink paint sample (b2) which contained a high proportion of sunflower oil ($\approx 13\%$ linseed oil, $\approx 70\%$ sunflower oil, $\approx 17\%$ safflower oil) differed from the blue paint sample ($\approx 66\%$ linseed oil, $\approx 23\%$ sunflower oil, $\approx 11\%$ safflower oil) (b3). The decrease for the pink paint heated at 50 °C was almost 20 % of the oil content within the first 6 h.⁷ Compared to the blue paint (4 %), which contained more linseed oil, this is very significant. Although part of the initial loss in weight may be related to evaporation of water it is likely that unlinked low molecular weight volatile fragments of the oil film were also lost.

SEM – BSE Analysis

The SEM-BSE images of a cryo cutted cross-section of a paint sample exhibiting a liquefied surface show a darker zone in the upper section (Fig. 4). This zone represents the liquefied area of the paint bulk approximately 150 μm thick. In both zones the same chemical elements were detected in a same relative concentration

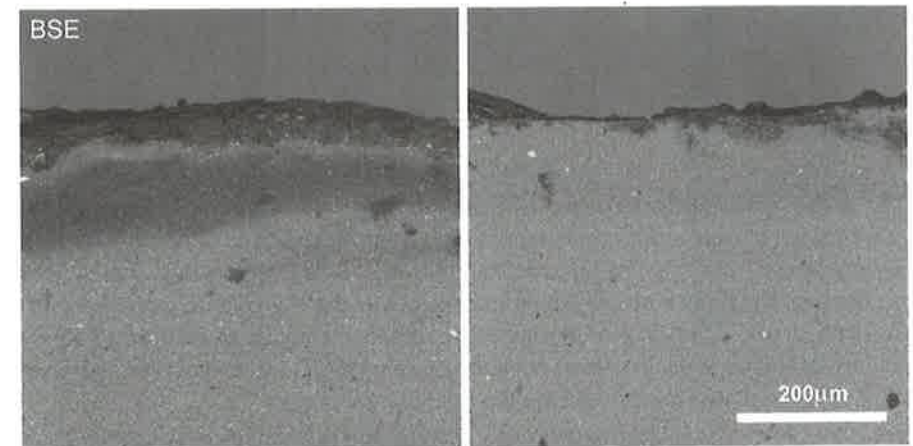


Fig. 4 SEM-BSE of a liquefied sample before (left) and after heat treatment at 80 °C for 24 h (right)

⁷Before analysis, samples were dried with silica gel for 7 days. The water content was determined for both samples and relates to the overall weight (blue: 0.18 %, pink: 0.23 %).

using energy-dispersive spectroscopy EDS, but in different amount (counts). The image contrast assessed from different elemental density using BSE indicates the presence of a higher concentration of organic material in the upper section. After thermal treatment this zone was hardened by evaporation of low molecular weight components to cause a change in pigment/volume concentration (Fig. 4).

FTIR Analysis

After thermal treatment of liquefied Buff Titanium paint Fourier transform infrared spectroscopy (FTIR) showed a slight shift of the $\nu(\text{C}=\text{O})$ stretch vibration of the esters at $1,745\text{ cm}^{-1}$ to lower frequencies what indicates the presence of other carbonyl groups (Fig. 5).⁸ These changes were already observed after 2 h of thermal treatment at $80\text{ }^{\circ}\text{C}$ and increased after 24 h of exposure. The spectrum changes described occurred after 2 h of thermal treatment and no considerable changes were detected in spectra taken from samples heated for 2 days. Though the process of hardening was not complete after 24 h only a certain increase in viscosity was evident in the sample. After 1, 2 and 5 days of thermal treatment at 40 and $60\text{ }^{\circ}\text{C}$ no changes could be detected in the FTIR spectra. The same spectral features were observed for the Buff Titanium sample (a1), which had already been hardened and was exposed for a month to a relative humidity of approximately 84 %. The sample exhibited a slight loss of hardness (needle test), which may partly relate to the formation of moisture equilibrium between the paint and the environmental conditions.

ESI-MS Analysis

The ESI – MS analysis spectrum of fresh sunflower oil (sample c3, high peak at m/z 903 of the triglyceride monomers) differs from the spectrum of running oil with drying defects (Fig. 6). The liquefied samples (a1 and a2) showed the presence of a variety of fractions with molecular masses below the triglyceride monomers (cf. Zumbühl et al. 2014a). This indicated the presence of a high amount of triglyceride fragments with a molecular mass between 200 and 900 Da. It reveals the relevance of the fragmentation reaction during the liquefying process.

⁸As a result of derivatisation with SF_4 very low molecular acids evaporate, since in the reaction product acryl fluoride there is no hydrogen-bond possible. Low molecular weight components were detected with GC-MS.

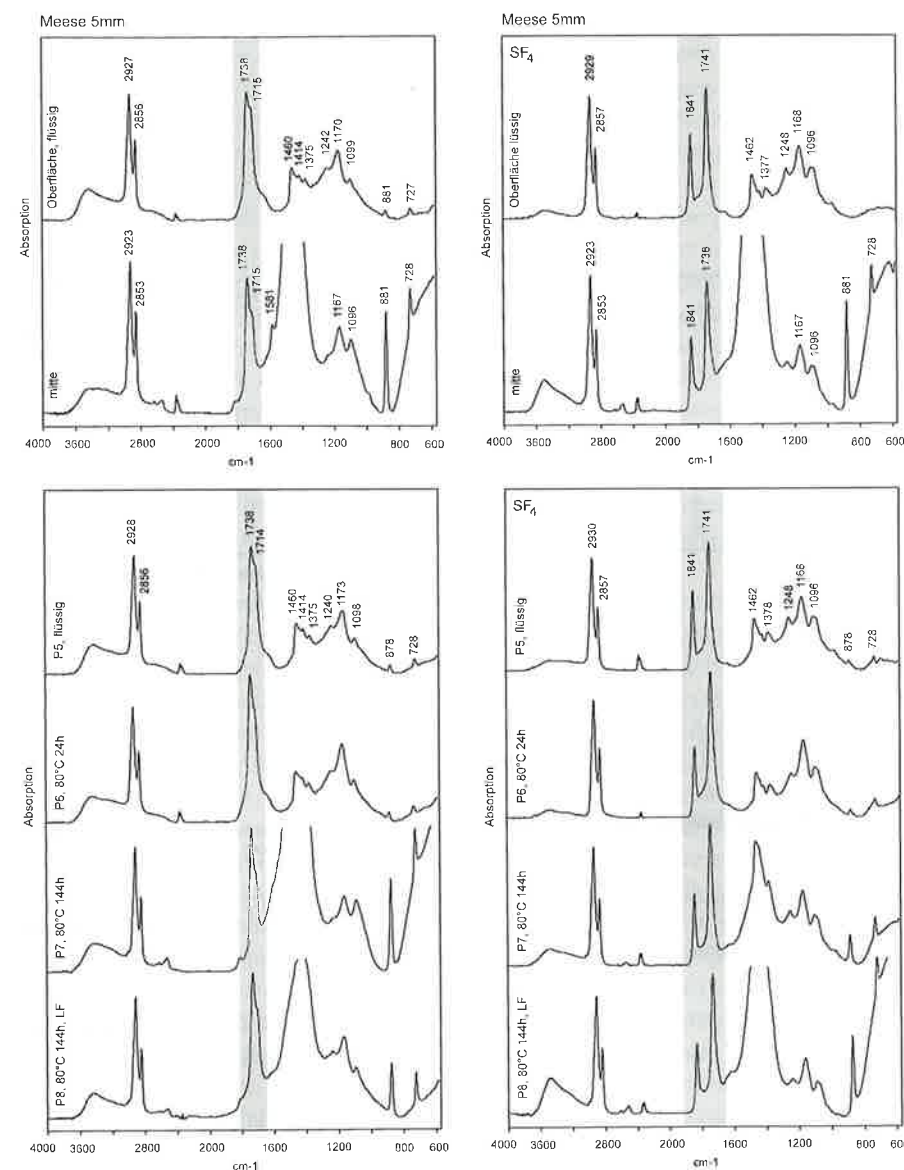


Fig. 5 FTIR spectra of a liquefied Buff Titanium sample before (left) and after (right) derivatisation using sulphur tetrafluoride before (top) and after (bottom) thermal treatment ($80\text{ }^{\circ}\text{C}/24\text{ h}$)

GC-MS Analysis

For the liquefied Buff Titanium samples (a1 and a2) the following ratio was detected: The azelate/sebacate (A/Seb.) ratio is around 11, the azelate/suberate

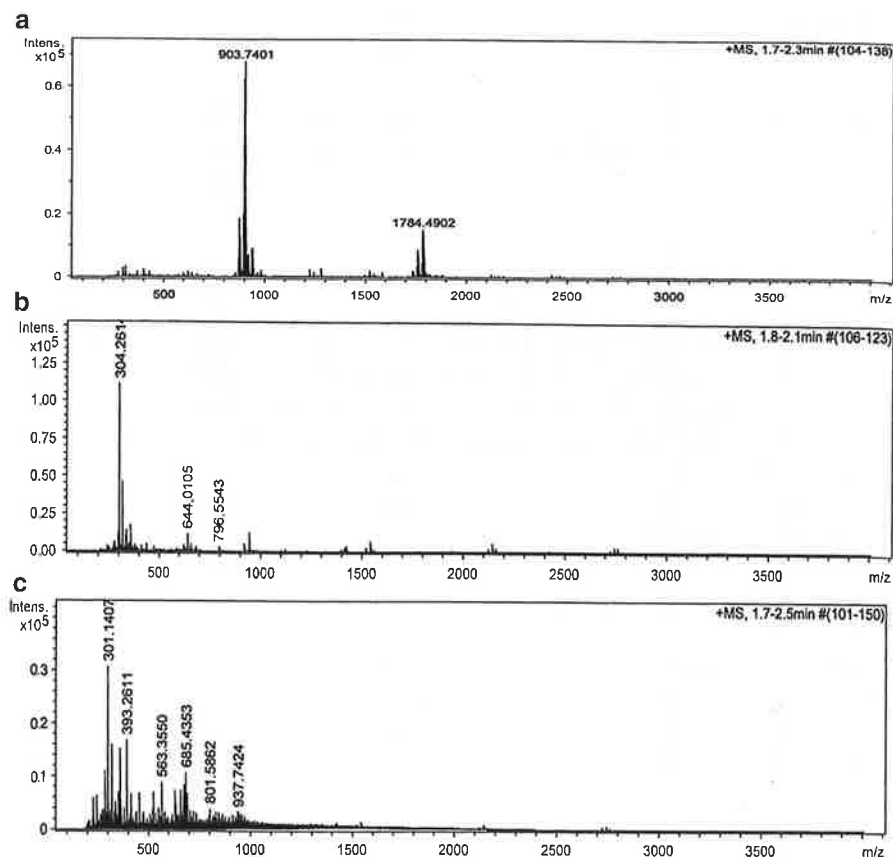


Fig. 6 ESI spectra positive mode, chloroform/methanol extract: (a) Fresh sunflower oil (sample c3, dilution 1:1,000) (b) Liquid phase Meese object (sample a1 + a2, dilution 1:100) (c) Liquid phase Meese object after 55 h by 80 °C (non-dilution)

(A/Sub.) ratio is around 3 and the palmitic acid/stearic acid (P/S) ratio is around 2.⁹ After thermal treatment the ratios have not changed significantly.¹⁰

Discussion

Hardening of liquefied oil paint samples (a1 and a2, b1) was successful when samples were exposed to temperatures between 70 and 80 °C. The degree of hardness was dependent on the temperature, the length of exposure and the film

⁹Qualitative fatty acid ratios of Buff Titanium samples before heat treatment: A/P: 0.6, A/Sub.: 2.7, A/Seb 11.1, P/S: 2.1, O/S: 0.1, Dihydroxy C18/S: 1.6.

¹⁰Qualitative fatty acid ratios of Buff Titanium samples after heat treatment (6 h 80 °C): A/P: 0.4, A/Sub.: 2.7, A/Seb.: 9.6, P/S: 1.9, O/S: 0.1, Dihydroxy C18/S: None.

thickness. Heat treatment at 40 and 60 °C even after 25 days did not change the viscosity of the paint significantly. This confirms the hypothesis that a minimum temperature of more than 60 °C is required for activating the process of hardening. The coalescence of the sample is only partly attributable to the heat exposure and results from the fact that the sample material assumes the most energy-efficient state.

Analytical results demonstrate that hardening is related to a loss in weight due to the volatilisation of low molecular compounds from the paint. Analysis of liquefied samples before and after thermal treatment could contribute to a deeper understanding of the mechanisms that lead to the complex liquefying process. ESI measurements and FTIR results confirm a large fragmentation of the liquefied paint. Based on the distribution of mass it can be inferred that the liquefied products of decomposition are for the most part fragmented triglycerides. GC-MS analysis indicated that heat treatment caused a reduction in dihydroxystearate as a possible hydrolysis product. FTIR and ESI analysis suggest that the paint became more acidic and polar on heating. It may be concluded that liquefaction results from significant oxidative fragmentation reactions and it can be inferred that the liquefied products of decomposition are for the most part fragmented triglycerides. Thus, the oil paint would not polymerise further or dry in the future.

The phenomenon of liquefaction was more pronounced in thicker paint. A critical thickness is necessary to allow separation of the binding medium to initiate the flow process to form drips. Paint samples containing larger amounts of sunflower oil (samples b2) degrade faster than paints with higher linseed oil content (samples b3), and they exhibit differences in acidity. Paints made using semi-drying oils are likely to exhibit more significant fragmentation by beta-elimination. As the hardening process on drying is dependent on the equilibrium between the formation and decomposition of peroxides, the consequences of the decomposition reaction are more apparent in semi drying oils. Semi drying oils have therefore a considerably reduced viscosity through ageing, which is why binding-medium components are able to settle on the surface as a fluid medium-rich layer.

The FTIR-results together with the TGA-measurements and SEM investigations show a consistent pattern: the weight loss in paint samples increased with heating time and at higher temperatures. Significant loss in weight at temperatures around 50 °C (without accompanying changes in viscosity) may partly be related to the evaporation of water. It can be assumed that significant amounts of the liquid component of the paint evaporate at higher temperatures. The liquid medium content decreases during thermal treatment and the pigment-binding medium ratio appears to be altered, due to the loss of volatile low molecular components, illustrated in the SEM – BSE images before and after heat treatment (Fig. 4). This is indicated by a reduction in the binding medium content in the FTIR spectrum, characterised by the change of the signal intensity relative to the carbonate absorption of the filler.

Analysis of liquefied paint samples after 24 h of heat treatment showed no difference between the liquefied areas on the surface and the deeper firmer paint in terms of acidity. As the signal intensity of the acyl fluoride in the IR-spectrum after selective derivatisation of the carboxylic acids (using SF₄) around 1,841 cm⁻¹ has not changed significantly the solid binding-medium components remain extremely acidic. Heating did not influence the polarity and degradation of the sample

material¹¹; instead the treatment primarily altered the pigment/binding media ratio. GC-MS analysis of samples before and after thermal treatment exhibited much the same chemical composition. Thus, the loss of a large single component cannot be confirmed.

Thermal treatment led to loss of volatile components but no significant changes in the polarity of the paint film. Thus, differences in acidity of the dicarbonic acids and the fatty acids have apparently no effect on the liquefaction process. Because of the large percentage of photochemical inert oxidation products no significant increase of oxidative cross-linking can be expected and so far no cross-linking reaction could be detected in treated samples. Therefore the hardening would appear primarily to be a physical process.

Conclusions and Perspectives

Analysis of liquefied samples before and after thermal treatment contributes to a deeper understanding of the mechanisms that lead to the complex liquefying process. The liquefaction of oil paint is primarily dependent on the type of oil. Case studies suggest that semi-drying oils – sunflower and safflower oil are one of the main causes of liquefaction. Since unpigmented sunflower and safflower oil may liquefy after 5 years it seems that pigments and additives have a less significant influence on this process.

This study showed that hardening of liquefied oil paint can be achieved by heating. However, a minimum temperature is required to activate the process of hardening. During heating low molecular components migrate and evaporate, leading to weight loss in the films. Thermal hardening of the liquefied paint is primarily a physical process.

Further studies of the process of liquefaction and hardening of liquefied oil-paint have been initiated that examine a range of samples including different pigments and binding media to observe the drying and liquefaction processes under various environmental conditions. Thus we hope to gain a better understanding of the influence of paint compositions, additives, and layer thicknesses as well as changing relative humidity and light exposure. Also, the long-term behavior of the thermally treated paint samples and in particular at higher relative humidity will be examined in more detail. Furthermore, methods will be developed on how to apply heat locally to a painting. A painting by Jonathan Meese with significant liquefaction defects presently serves to develop a strategy and to evaluate an effective treatment.

¹¹During SF₄ treatment carbonates like lead carbonate or calcium carbonate are converted into fluorides, which are not IR active. Therefore no interference is shown on the spectra after derivatisation. However dolomite is stable under dry derivatisation conditions. Therefore the Buff Titanium samples continue to show the signals from the bulking material.

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Appendix

Instrumentation, materials and suppliers

Film application

Feeler gauge, 2 mm (Vogel Germany GmbH & Co. KG)

Support (paint and oil samples)

Microscope slides (Carl Roth GmbH + Co. KG)

Polycarbonate film, translucent, colourless (Modulor GmbH)

Heat treatment

Laboratory oven UM 100–800 (Mettler)

Data logger

Thermofox Universal with Multisensor and Thermoelement System, Hygrofox with Universal HUB (Scantronik Mugrauer GmbH)

Results were processed using SoftFOX software

EL-USB-2, results were processed using EasyLog USB software (Lascar Electronics Ltd.)

Storage at high humidity

Potassium chloride (Carl Roth GmbH + Co. KG)

Microscopy

VHX-500FD digital microscope (Keyence)

Leica MZ Fluo microscope (visible light and BP 420-490), results were processed using Diskus software (Carl H. Hilgers)

Gravimetry

Analysis balance (Sartorius AG)

GS – MS: Sample preparation and conditions

Samples were derivatised using 20 µL Meth-Prep II (Alltech, UK) and heated for 1 h at 60 °C, then cooled to room temperature overnight.

GCMS analysis was carried out on a Varian Saturn CP-3800 GC coupled with a 1,200 L MS detector.

Column: Phenomenex DB5-MS; 30 m × 0.25 mm × 0.25 µm.

Oven program: held at 50 °C for 1 min then ramped to 320 °C at 10 °C/min then held for further 5 min at 320 °C.

Splitless injection volume of 1 µl.

Helium flow of 1.5 ml/min.

MS conditions: Source temp: 200 °C; transfer line: 300 °C, solvent delay of 9 min. EI mode (70 eV); scan group 1: 45–300 amu; Group 2: 45–700 amu at 16 min, every 1 s.

Results were processed using Varian Workstation software, version 6.8.

ESI-MS: Sample preparation and conditions

ESI mode: Positive; 50 bis 4,000 m/z; 2 GHz

Instrument: Bruker maXis 4G

Samples were extracted by chloroform/methanol (2:1) mixture and diluted with methanol (up to 1:1,000). Spectra are measured by institute for organic chemistry, University Duisburg-Essen.

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