

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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Cultural Heritage Agency
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Editors

Klaas Jan van den Berg
Matthijs de Keijzer
Alberto de Tagle
Cultural Heritage Agency of the Netherlands
Amsterdam, The Netherlands

Jay Krueger
National Gallery of Art
Washington, DC, USA

Gunnar Heydenreich
Cologne Institute of Conservation Sciences
Cologne University of Applied Sciences
Köln, Germany

Aviva Burnstock
Department of Conservation and Technology
The Courtauld Institute of Art
London, UK

Tom Learner
Science Department
The Getty Conservation Institute
Los Angeles, CA, USA

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

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

References

- Brachert T (1985) Patina: von Nutzen und Nachteil der Restaurierung. Callwey, München
- Daudin-Schotte M, Bisschoff M, Joosten I, van Keulen H, van den Berg KJ (2013) Dry cleaning approaches for unvarnished paint surfaces. In: Mecklenburgh M (ed) Proceedings from of the cleaning 2010 conference, Valencia, 26–28 May 2010. Smithsonian Institute, pp 209–219
- Dobbels D (2000) Nicolas de Staël. Hazan, Paris
- Paris Central (2009) Vrije stad, vrije kunst in de jaren'50, Cobra Museum voor Moderne Kunst Amstelveen, 2009, exhibition catalogue

Derivatisation Technique for Infrared Spectroscopy – Characterisation of Oxidative Ageing Products in Modern Oil Paint

Stefan Zumbühl, Nadim C. Scherrer, and Wolfgang Müller

Abstract In conservation science the Fourier transformed based infrared spectroscopy (FTIR) is a standard technique to the study of historic paint layers. There are, however, clear limitations when analysing modern oil paint. The spectral information of aged oils is affected from overlapping signals of the binder, the oxidative ageing products, soaps formed during ageing, as well as several pigments and fillers. The distinction of the ageing products such as ketone and carboxylic acid functional groups pose the next problem, as these interfere with the triglyceride esters. Gaseous sulfur tetrafluoride SF₄ was used to discriminate overlapping signals in aged oil paint. This derivatisation technique makes it possible to convert carboxylic acids and carboxylate salts into acyl fluoride, while ketones and ester groups remain intact. IR spectra after SF₄ treatment show a characteristic splitting of the carbonyl band, allowing the characterisation of the different functional groups formed during oxidative ageing. Furthermore, it is possible to increase the spectral selectivity thanks to the successful elimination of spectral interferences caused by organometallic and inorganic compounds. This sample pre-treatment can be applied to both micro-samples and polished cross-sections, enabling 2D localisation of these compounds in aged oil paint samples using infrared imaging FTIR-FPA (focal plane array). Both artificially aged and real paint samples of twentieth century paintings were investigated to characterise degradation processes in oil paint, including the dripping phenomenon of modern oil paints.

Keywords Infrared spectroscopy • Infrared imaging • Overlapping signals • Derivatisation technique • Sulfur tetrafluoride • Acyl fluoride • Liquefied paint • Sunflower oil • Safflower oil

S. Zumbühl (✉) • N.C. Scherrer
Bern University of Applied Sciences, Fellerstrasse 11 CH-3027, Bern, Switzerland
e-mail: stefan.zumbuehl@bfh.ch; nadim.scherrer@bfh.ch

W. Müller
H. Schmincke & Co. GmbH & Co. KG, Otto-Hahn-Str. 2, D-40699 Erkrath, Germany
e-mail: mueller@schmincke.de

Introduction

Fourier Transform infrared spectroscopy (FTIR) is a long established standard technique in conservation science (Derrick et al. 1999). With the arrival of 2D FTIR-FPA imaging at a spatial resolution down to 1 micron, this analytical technique is reaching even more analytical power. For example, it makes it possible to identify and localise organic compounds *in-situ* within micro-samples. But there are clear limitations to FTIR when analysing binding media in paint samples. For example, the interpretation of standard infrared spectra on modern oil paint samples suffers from overlapping signals of the binder, the oxidative ageing products, soaps formed during ageing, as well as several pigments and fillers. The chemical alteration of oil paint is a complex process due to interdependent chemical reactions running either simultaneously or sequentially (Zumbühl et al. 2011). The chemical pathways are well investigated and described in several overviews (Kamal-Eldin 2003; Frankel 1998; Chan 1987; Richardson and Korycka-Dahl 1984). Of particular interest in this context are oxidative cross-linking reactions, oxidative fragmentations, hydrolysis, and soap formation (Van den Berg 2002; Van den Berg et al. 1999). All these different reactions lead to various functional groups producing characteristic IR-absorptions. With respect to the interpretation of ageing products, standard FTIR spectroscopy faces a fundamental problem due to interfering signals from all the oxidation products such as ketones and carboxylic acids with the oil triglyceride esters. Additionally, artist's paints are complex material systems containing colorants, mineral fillers and different kinds of additives, all contributing to the spectral signal. In order to improve the selectivity of the FTIR technique with respect to the study of the oxidative ageing products in modern artist's oil paints, an additional sample preparation step was introduced to selectively derivatise specific compounds or functional groups, applicable both to micro-samples (μ -FTIR) and polished cross-sections (2D FTIR-FPA imaging) (Zumbühl et al. 2014).

Derivatisation with Sulfur Tetrafluoride SF₄

The selective alteration of functional groups using reactive gases is an established technique and was introduced for the FTIR analysis of oxidation products in polymeric materials (Wilhelm and Gardette 1994; Mailhot and Gardette 1992; Carlsson et al. 1988). The same technique was used by Mallécol et al. for the characterisation of the reaction products formed after peroxide homolysis in non-pigmented drying oils (Mallécol et al. 1999, 2000a, b, c). The reagent SF₄ reacts selectively with carboxylic acids R(O)OH to form an fairly stable acyl fluoride R(O)F, leading to a characteristic splitting of the carbonyl band. The conversion of the carboxylic acids into acyl fluoride leads to a shifted carbonyl vibrations $\nu(\text{C}=\text{O})$ at 1,841 cm⁻¹, while ketone $\nu(\text{C}=\text{O})$ at \approx 1,720 cm⁻¹ and ester $\nu(\text{C}=\text{O})$ at \approx 1,740 cm⁻¹ groups remain intact (Wilhelm and Gardette 1994).

Moreover, the elimination of the carboxylic O—H signal makes it possible to detect alcoholic hydroxyl functionalities $\nu(\text{O—H})$ [br] at \approx 3,500 cm⁻¹ selectively (Zumbühl et al. 2014). This makes it possible to investigate the formation of carboxylic acids during oxidation and hydrolysis. Besides the interferences by organic compounds mentioned above, there are further overlapping bands generated by inorganic pigments and fillers. Furthermore, ageing will generate organometallic reaction products formed between the binder molecules and the cations of the pigments. These are known to stabilise the aged binder network (Van den Berg 2002; Van den Berg et al. 1999). The dominant changes during ageing are due to the soap formation, causing broad signals of the carboxylates at around \approx 1,600 cm⁻¹ $\nu_a(\text{C}(\text{O})\text{O}^-)$ [s], \approx 1,450 cm⁻¹ $\nu_s(\text{C}(\text{O})\text{O}^-)$ [m-s] and \approx 850 cm⁻¹ $\nu_{\text{sc}}(\text{C}(\text{O})\text{O}^-)$ [m] (Socrates 2004) covering the signals from the fatty acid backbone at 1,464 cm⁻¹ $\delta(\text{CH}_2)$ [s], 1,378 cm⁻¹ $\text{wag}(\text{CH}_2)$ [m] and 1,418 cm⁻¹ $\text{wagR}(\text{C—H}_2)\text{—C}(\text{O})\text{O}^-$ [m] (Lazzari and Chiantore 1999; Meilunas et al. 1990). Applying this derivatisation to aged oil paint samples makes it possible to eliminate these signals, since soaps such as zinc or lead carboxylates R(O)OM are transformed into acyl fluoride R(O)F (Zumbühl et al. 2014). Furthermore, pigments such as the often used lead white exhibits a dominant and broad signal of the CO₃⁻² ion ν_3 at \approx 1,400 cm⁻¹ [ν_s] (Meilunas et al. 1990; White 1974), which strongly limits the observation of the organic binder compounds in paint samples. Using the SF₄ derivatisation technique, the basic lead carbonate 2PbCO₃·Pb(OH)₂ can be transformed into the non-IR active lead fluoride β -PbF₂ (Zumbühl et al. 2014). Following the treatment, the signals of the pigment are no longer present and the IR spectrum of the oil binder is free of disturbing signal overlaps (Fig. 1).

Application of the Derivatisation Technique

With the spectral elimination of alteration products and pigments in paint micro-samples, the identification of complex binder systems is possible. One focus was set on the formation of different oxidation products and the characterisation of the material polarity during natural and accelerated ageing of oil paint (Zumbühl et al. 2011). This is of interest because the chemical pathways are strongly influenced by the paint formulation and the variable ageing conditions. Being able to detect minor binder components within the 2D structure of drying oil based paint is a very powerful research tool. The SF₄ derivatisation technique was successfully applied to the detection of small protein concentrations in tempera paint (Zumbühl et al. 2014). The investigation of such emulsified systems made of oil and protein is not possible with standard FTIR, as the broad bands of the carboxylate anion $\nu_a(\text{C}(\text{O})\text{O}^-)$ at \approx 1,600 cm⁻¹ (ageing products) interfere with the protein bands amide I ($\nu(\text{C}=\text{O})$) at \approx 1,650 cm⁻¹ and amide II ($\delta(\text{N—H})$ and $\nu(\text{N—C})$) at \approx 1,540 cm⁻¹. Furthermore, the amide II band can be superimposed by the very broad and strong band of the carbonate CO₃⁻² anions $\nu_3 \approx$ 1,400 cm⁻¹ generated by pigments or fillers. Besides the derivatisation of micro-samples, this pre-treatment can also be

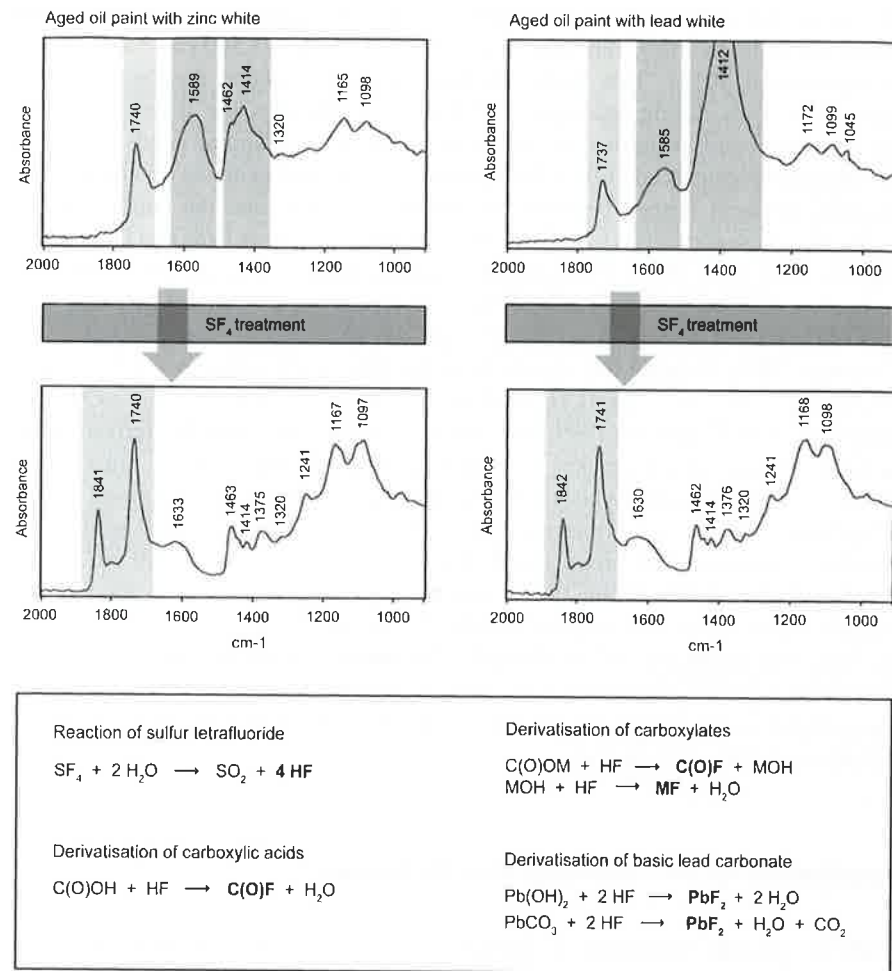


Fig. 1 Derivatisation of 60-year old oil paint films before (*upper*) and after SF₄ treatment (*lower*). Interference of the soaps and the pigments is eliminated (*dark grey*). The different carbonyl groups are now visible as separated bands (*grey*)

applied to polished cross-sections or surfaces (Zumbühl et al. 2014). The technique allows research on the interrelationships of such complex material systems within the original stratigraphic structure. 2D studies on the intact morphology disclose a great deal more information than detached sample analysis with destroyed context. By applying this derivatisation technique in combination with FTIR-FPA (focal plane array) imaging to paint cross-sections, it is possible to map the binder components within a paint layer at a spatial resolution of 1–1.5 μm. An example is presented in Fig. 2, where it was possible to image the oxidation gradient in a modern oil paint film. The reaction of SF₄ is superficial and the penetration

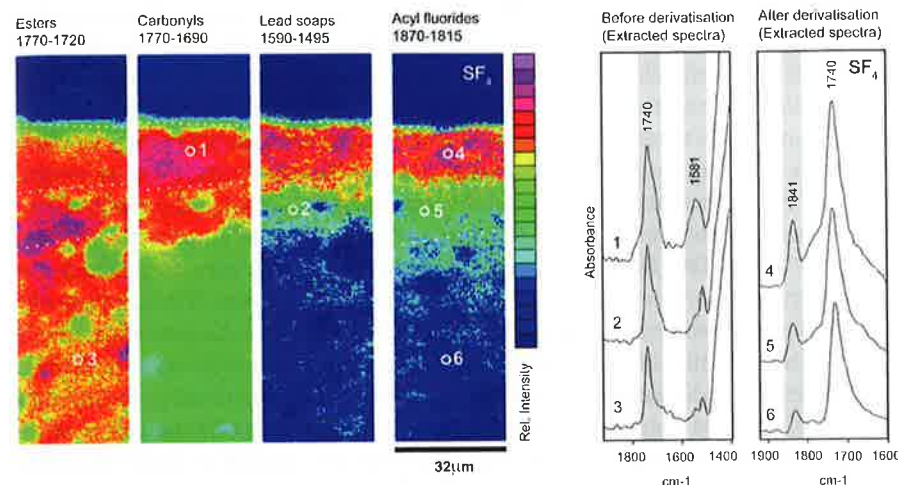


Fig. 2 Derivatisation of oil paint containing lead white. The FTIR-FPA imaging before and after treatment with SF₄ delivers information on the spatial distribution of the different oxidation and degradation products formed within a paint layer

depth at maximum a few microns deep so that samples can easily be repolished to remove the derivatised surface layer. The penetration depth using ATR technology in organic layers ($\approx n_D 1.5$) using a germanium crystal ($n_D 4.0$, beam angle 45°) is in the range of 0.2–0.7 μm, meaning that a reaction depth of 1 μm is sufficient for the method to work successfully (Zumbühl et al. 2014). The standard reaction time of 24 h was in all cases sufficient to achieve an ubiquitous and homogeneous derivatisation across the surface. The present work has applied this derivatisation technique to characterise different functional groups within a paint layer in order to gain information on the drying process of modern oil, including dripping oil paint.

Experimental

Sulfur tetrafluoride SF₄ (ABCR® Dr. Braunagel GmbH & Co. KG, Art No. AB10417) treatment in gas phase was used to derivatise different kinds of oil paint micro-samples as well as cross-sections. The micro-samples were rolled on to a CVD diamond window prior to placement into the gas reaction chamber. Stratigraphic samples were embedded in epoxy resin Araldite 2020 (2 component XW396/397) and sections were prepared using dry polishing cloths of the type Micro-mesh®. The derivatisation treatment using the active gas SF₄ was performed in an all-*teflon*® chamber (volume 10 cm³) (Carlsson et al. 1988; Mallégo et al. 2000c). All samples were exposed to the SF₄ gas at room temperature for 24 h. Before and after the reaction, the chamber was flushed with nitrogen N₂ and the eliminated

gas was adsorbed to active charcoal. FTIR measurements were performed on a Bruker® Hyperion 3000/Tensor 27 infrared spectrometer with a germanium ATR crystal (\varnothing 250 mm). The pixel resolution is 0.5 μm with the FPA detector made of 64×64 detector elements, covering an area of $32 \times 32 \mu\text{m}$. Micro-samples were analysed in transmission mode at 4 cm^{-1} spectral resolution and 32 scans. The 2D FTIR-FPA imaging was performed in ATR mode at 8 cm^{-1} spectral resolution and 64 scans. More details can be found in (Zumbühl et al. 2014). The electrospray ionisation mass spectrometric ESI-MS measurement was performed with a Bruker maXis 4G UHS-TOF (Ultra High Resolution Time of Flight) mass spectrometer at the University Duisburg-Essen (Institute for Organic Chemistry). The samples was extracted in a chloroform / methanol mixture and measured in the positive mode.

To investigate the oxidation gradients in very thick paint layers, accelerated ageing tests were performed. The paint products used were linseed oil paint (Kremer GmbH & Co. KG) containing basic lead white (Kremer 460007) and zinc white (Kremer 463207) without dryer content. The paint was applied at a film thickness of 2 mm to a silicon-coated Hostaphan®-Foil RNT 36 (Kremer GmbH & Co. KG) and pre-dried in darkness under room condition ($23 \text{ }^\circ\text{C}/50\%\text{RH}$) for 1 week. The samples were aged under window glass filtered fluorescence light (True Lite® 5500 K and Philips® UV-20 W/08 F20 T12 BLB generating $\approx 5,800 \text{ lm/m}^2$, $557 \text{ mW lm}^{-1}/\approx 3,200 \text{ mW/m}^2$) at $\approx 40 \text{ }^\circ\text{C}$, $55\%\text{RH}$ and atmospheric oxygen content over a time period of 6 weeks. To investigate the dripping process of oil paint (applied in thick layers), different paint samples were produced in 2003 by H. Schmincke & Co. GmbH & Co. KG, Erkrath (Germany) according to paint formulation of 1994. The paint was applied in variable thickness up to 5 mm on a paint board. The binder of the blue paint (Prussian blue) contains $\approx 66\%$ linseed oil, 23% sunflower oil and 11% safflower oil. The binder of the light pink paint (titanium dioxide and cadmium pigments) contains $\approx 13\%$ linseed oil, $\approx 70\%$ sunflower oil and $\approx 17\%$ safflower oil. The light pink paint contains Co- and Zr-dryer, whereas the blue paint is free of additives. Pure oil samples used in paint formulation of 1994 were applied at a thickness of $60 \mu\text{m}$ in 2005 (vertical store of the paint board results in slots of the oils). All samples were aged under room conditions. A sample of liquefied paint was taken from a 10 years old painting by the German artist Jonathan Meese.

Results and Discussion

Ageing of modern oil paint is fundamentally different to ageing of the classical paint systems. This is strongly related to the material composition of modern artist's paints. On the one hand, the ageing process is strongly influenced by the binder composition. Modern oil paints often consist of a variable mixture of different oils in order to control the drying behaviour of the different colours. In addition to this, general regulations with respect to the quality and stability modern pigments have changed. As a result, modern oil paints exhibit a different degradation

behaviour when compared to classical oil paints. There is an increasing number of incidents where such modern paints liquefied within a few years after application (in thick layers) and drying (see Boon and Franken et al. in this contribution). This phenomenon was observed both in oil paint and in binder samples applied without pigments, fillers or additives. It can thus be assumed that the process is related to the binder composition. All incidents of paint liquefaction upon ageing so far were related to a high content of sunflower and/or safflower oil. To achieve a characterisation of these cases, SF_4 sample pre-treatment in combination with FTIR spectroscopy came into application. Since drying oils are highly oxidative, the ageing of oil leads to characteristic changes in the IR spectra. The kind of stable functional groups formed is of direct relevance to predict a specific ageing behaviour (Mallégol et al. 1999). A comparison of two sample paints out of the same product series having variable oil composition, permits to draw preliminary conclusions on specific degradation processes. While the first paint (blue) is bound with $\approx 66\%$ linseed oil, the second one has been made with $\approx 87\%$ sunflower and safflower oil (light pink). These two paints exhibit a completely different ageing behaviour: while the linseed oil based paint is still solid after 7 years of natural ageing, the sunflower/safflower oil bound paint has liquefied.

In both samples, the increase in oxidation products is evident in the FTIR spectra from the formation of carbonyl groups $\nu(\text{C}=\text{O})$ [vs] within $1,720\text{--}1,740 \text{ cm}^{-1}$ in varying extent. But the softened paint shows a distinctive splitting of the $\nu(\text{C}=\text{O})$ peak. FTIR results suggest that distinct reaction pathways are evident and that different functional groups are being formed during oxidation. An increase of the $\nu(\text{C}=\text{O})$ carbonyl intensity refers to new carbonyl containing functional groups. Furthermore, a broadening of the triglyceride ester signal $\nu(\text{C}=\text{O})$ [vs] ($\approx 1,720\text{--}1,740 \text{ cm}^{-1}$), forming a shoulder at higher frequencies ($\approx 1,770 \text{ cm}^{-1}$), indicates the formation of lactones, whereas a broadening to lower frequencies ($\approx 1,700\text{--}1,720 \text{ cm}^{-1}$) indicates the formation of ketones and carboxylic acids (Mallégol et al. 2000a; Meilunas et al. 1990). After selective fluorination of the carboxylic acids groups during derivatisation with SF_4 , the intensity of the $\nu(\text{C}=\text{O})\text{F}$ absorption at $\approx 1,840 \text{ cm}^{-1}$ is an indicator for the acidity of the aged paint. It is evident, that the sunflower and safflower rich oil paint is much more acidic than the linseed oil paint (Fig. 3). The corresponding analysis of the dripping phase of aged oil paints and the liquefied pure oils all showing a very high carboxylic acid content (high signal intensity of the acyl fluorides at $\approx 1,840 \text{ cm}^{-1}$ relative to the ester band at $\approx 1,740 \text{ cm}^{-1}$). Moreover, the elimination of the carboxylic O—H signal during fluorination of the acids makes it possible to detect the alcoholic hydroxyls $\nu(\text{O}—\text{H})$ [br] at $\approx 3,500 \text{ cm}^{-1}$ selectively. Since there are no significant hydroxyl absorptions present in the liquid oil phase (Fig. 4), it can be concluded that the carboxylic acids are mainly formed during oxidation rather than during hydrolysis.

The formation of carboxylic acid groups is caused by the fate of thermo semi-stable peroxides $\text{R}—\text{O}—\text{O}—\text{R}'$ formed during oxidation (Fig. 5) (Mallégol et al. 2000a). The homolytic cleavage of these primary reaction products leads to the formation of alkoxy radicals $\text{R}—\text{O}\cdot$, which initiate different kinds of secondary

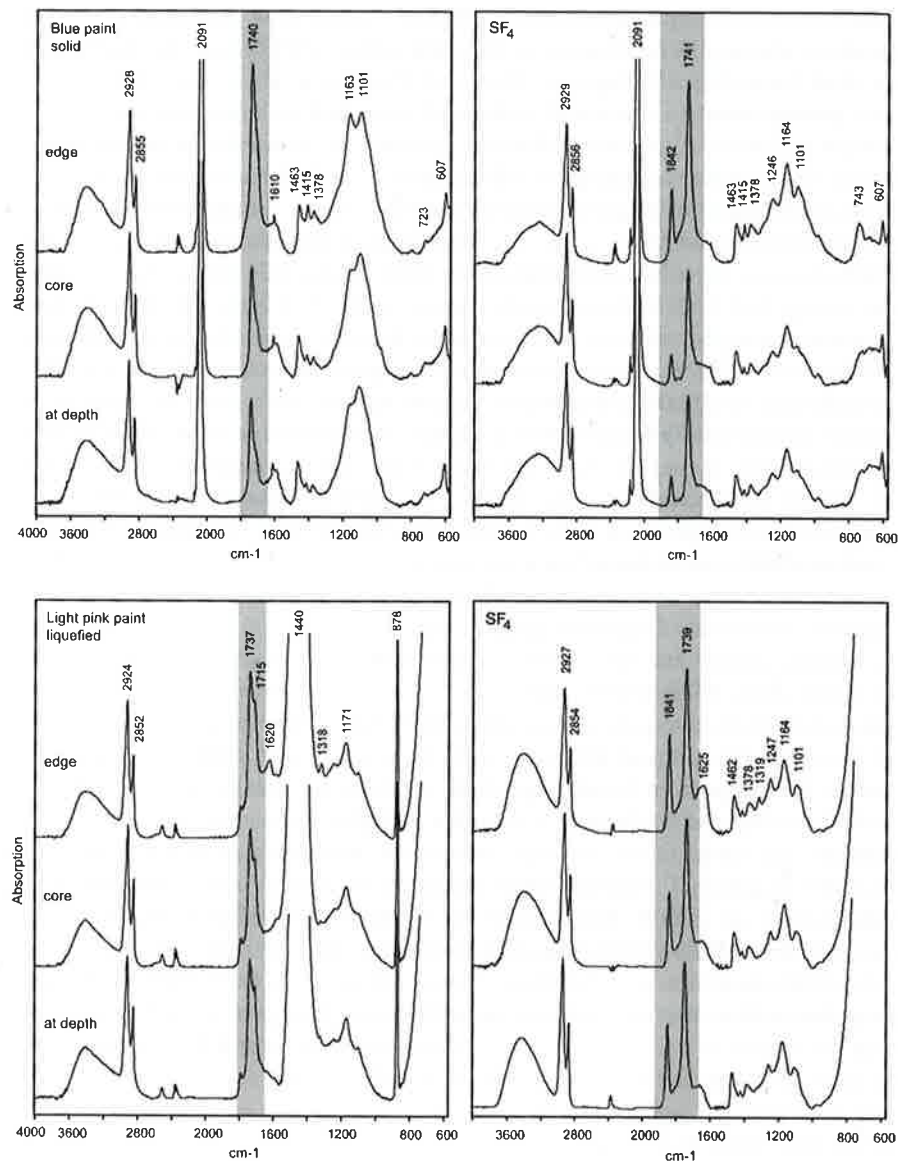


Fig. 3 Infrared spectra before (*left*) and after derivatisation with sulfur tetrafluoride (*right*). The upper spectra represent a solid paint rich in linseed oil, whereas the lower series represents paint rich in sunflower/safflower oil that has liquefied. Applying SF₄ derivatisation removes signal interferences and reveals the carbonyls as split bands (*grey*). The signal response of the acylfluoride at 1,840 cm⁻¹ suggests that the liquefied paint contains a lot of carbonic acids

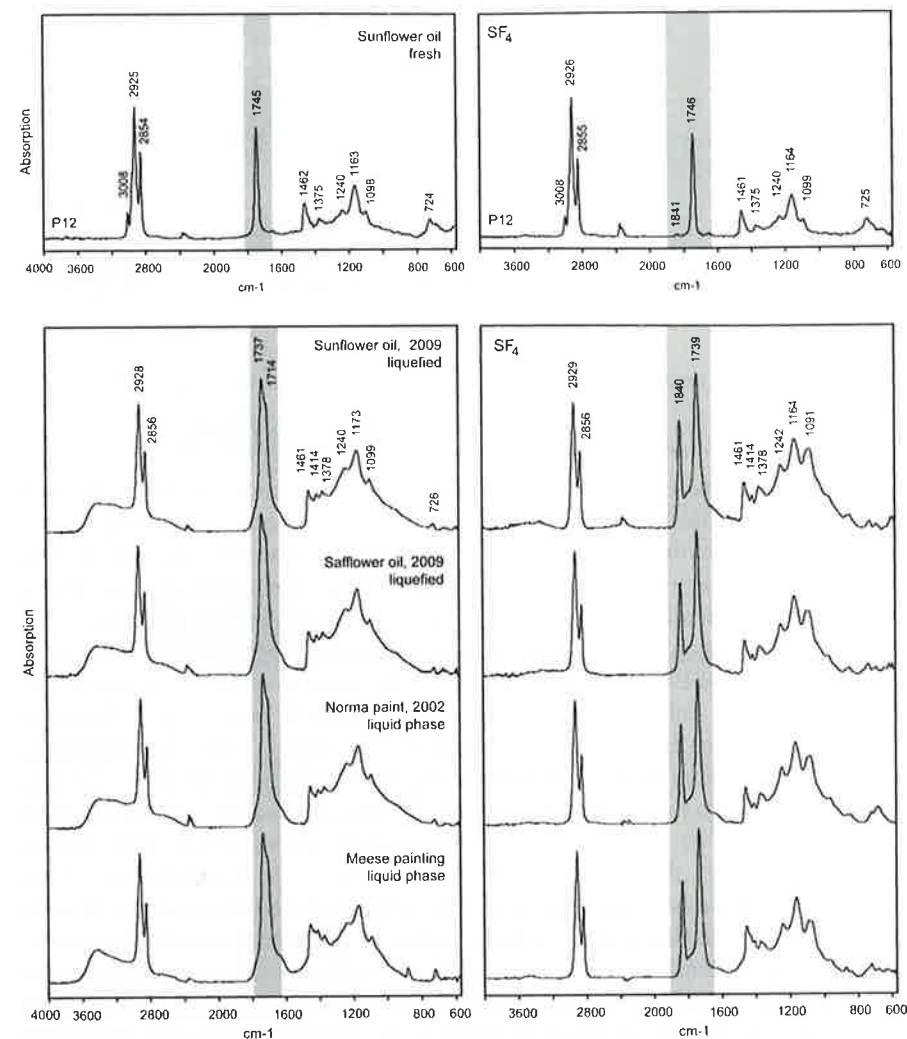


Fig. 4 Infrared spectra of liquefied oils before (*left*) and after derivatisation with SF₄ (*right*). The derivatised sample reveals the carbonyls as separate groups, with the acylfluoride at 1,840 cm⁻¹ pointing at a very high content of carbonic acids

reactions (Malléjol et al. 2000a; Gladovic et al. 1997; Chan 1987; Gardner 1987; Grosch 1987; Schieberle et al. 1984). The peroxide homolysis can be induced by temperature and may be assisted by metal catalysts (Van den Berg 2002; Malléjol et al. 2000b; Black 1978; Bawn 1957; Morley-Smith 1957; Banks et al. 1954). The degradation of unsaturated oils is fundamentally caused by the β -elimination (fragmentation reaction), which is the dominant reaction pathway at room temperature (Malléjol et al. 2000b, c; Lazzari and Chiantore 1999; Chan 1987;

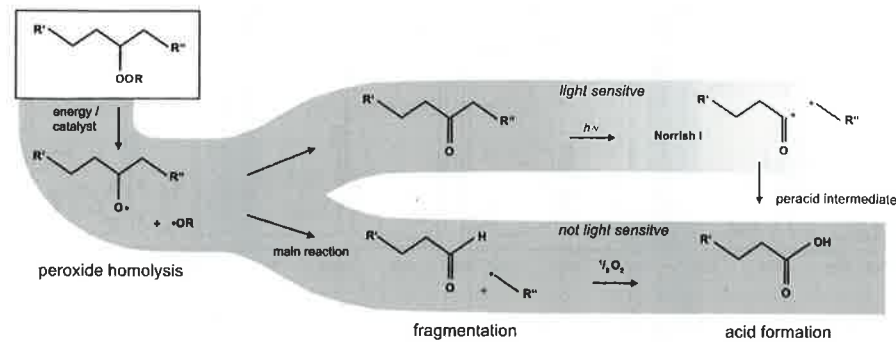


Fig. 5 Survey of the reaction pathways of lipid oxidation and fragmentation as described in the literature

Grosch 1987; Muizebelt 1978). The implication of this reaction can also be derived from the high content of oxalates, as oxalic acid is generated similarly by the decomposition of hydroperoxides of oxidised double bonds. Our data indicate that this kind of degradation process is a particularly distinctive feature of semi-drying oils. The process finally ends in the total fragmentation of the fatty acid chains and the parallel formation of end-standing carboxylic acid groups (Fig. 5) (Zumbühl et al. 2011; Kamal-Eldin 2003; Chan 1987). In classical oil paint, however, the increase in acidity enhances the formation of carboxylate salts (soaps) (Zumbühl et al. 2011; Van den Berg 2002; Van den Berg et al. 1999). These organometallic reaction products are important to stabilise the aged triglyceride network (Van den Berg 2002; Van den Berg et al. 1999). In the presence of bivalent cations, this kind of cross-links can be formed. In absence of a cation source, which often applies to modern oil paint, the fragmentation reaction induces the destabilisation of the network and a decrease of the molecular mass of the triglyceride molecules. In semi drying oils, this reaction leads to a large variety of liquid triglycerides fragments. This molecular decomposition in sunflower and safflower oil was confirmed by electrospray ionisation mass spectroscopy ESI-MS. In contrast to the non-liquefied paint the liquid phases contain high amounts of compounds with low molecular masses below the fatty acid triglyceride molecules (200–900 Da) (Fig. 6). The chemical nature of these liquid triglycerides fragments was not investigated in more details. Furthermore, thermogravimetric TGA measurements showed, that up to 30 % of the binder content can be evaporated within 24 h at no more than 50 °C, indicating a high amount of comparable low molecular weight oil compounds. In contrast the amount of volatilise compounds in the linseed oil rich paint is comparable low (see Franken et al. in this contribution). Even though the fragmentation of the fatty acids is common to all oils, the implications on the complete system are strongly dependent on the type of oil. The network properties are influenced on the balance between stabilising and destabilising reactions. The possibility of recombination of radicals in poorly unsaturated oils is structurally limited and the density of cross-linking is reduced. The decomposition of peroxides

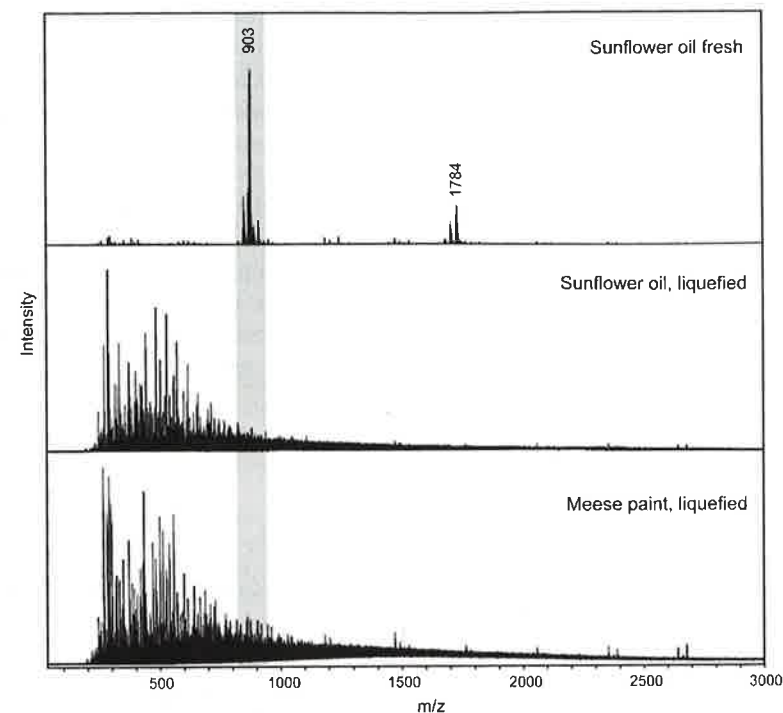


Fig. 6 The electrospray ionisation mass spectra (ESI-MS) demonstrate, that aged sunflower oil is fragmented into lots of triglyceride fragments with masses below the triglyceride monomers (*grey*). A comparable MS pattern was found in a liquefied painting by Jonathan Meese

thus will have a stronger influence on the material properties. Aggravating to this situation will be the potentially increased demand on siccatives with semi drying oils to achieve efficient drying. Those will have a negative influence on the ageing behaviour, as these catalysts decompose peroxides very effectively and as such also act as catalysts in the degradation process. As a result of this, colours with semi drying oils as binder, in thick layers applied, may liquefy after a few years. From this we can infer, that the degradation behaviour of modern oil paint is strongly controlled by the binder composition.

Conclusion

A major drawback of infrared spectroscopy FTIR is the poor selectivity in complex material systems due to signal interferences of different functional groups within similar spectral ranges. Furthermore, signal interferences with the oil binder are caused by oxidative ageing products and carboxylate salts formed during ageing,

as well as several pigments and fillers. This is of great limitation, in particular to the study of modern oil paint. Sample pre-treatment with sulfur tetrafluoride SF₄ to derivatise certain compounds substantially increases the selectivity of the IR technique by eliminating signal overlaps. The method allows the spectral separation of carbonyls of different functional groups and the elimination of signal interferences caused by ageing products, pigments and fillers. This derivatisation technique was applied in the present case in particular to document the acidity of the different aged oils. The data was used to gain information on potential degradation mechanisms in modern oil paint. As demonstrated, the SF₄ technique considerably enhances the power of standard FTIR and is of great relevance to art conservation science. Its applicability to polished cross-sections in combination with high resolution 2D FTIR-FPA imaging can be regarded as a fundamental advancement.

References

- Banks GL, Chalk AJ, Dawson JE, Smith JF (1954) Catalysis of olefin autooxidation by heavy-metal ions in non-polar media. *Nature* 174:274–275
- Bawn CEH (1957) The role of peroxidic catalysts in coating compositions. *J Oil Colour Chem Assoc* 40:1027–1034
- Black JF (1978) Metal-catalysed autooxidation – the unrecognized consequences of metal-hydroperoxide complex formation. *J Am Chem Soc* 100(1):527–535
- Carlsson DJ, Brousseau R, Zhang C, Wiles DM (1988) Chapter 27: Identification of products from polyolefin oxidation by derivatization reactions. In: Benham J, Kinstle JF (eds) *Chemical reactions on polymers*. ACS symposium series 364. American Chemical Society, Washington, DC, pp 376–389
- Chan HW-S (1987) *Autooxidation of unsaturated lipids*. Academic, London
- Derrick MR, Stulik D, Landry JM (1999) *Infrared spectroscopy in conservation science. scientific tools for conservation*. The Getty Conservation Institute, Los Angeles
- Frankel EN (1998) *Lipid oxidation*. The Oil Press LTD, Dundee, Scotland
- Gardner HW (1987) Reactions of hydroperoxides – products of high molecular weight. In: Chan HW-S (ed) *Autooxidation of unsaturated lipids*. Academic, London, pp 51–93
- Gladovic N, Zupancic-Kralj L, Plavec J (1997) Determination of primary oxidation products of linoleic acids and triacylglycerols. *J Chromatogr A* 767:63–68
- Grosch W (1987) Reactions of hydroperoxides – products of low molecular weight. In: Chan HW-S (ed) *Autooxidation of unsaturated lipids*. Academic, London, pp 95–149
- Kamal-Eldin A (2003) *Lipid oxidation pathway*. AOCS Press, Champaign
- Lazzari M, Chiantore O (1999) Drying and oxidative degradation of linseed oil. *Polym Degrad Stab* 65:303–313
- Mailhot B, Gardette J-L (1992) Polystyrene photooxidation – I. Identification of the IR-absorbing photoproducts formed at short and long wavelengths. *Macromolecules* 25:4119–4126
- Mallégol J, Gardette J-L, Lemaire J (1999) Long-term behavior of oil-based varnishes and paints – I. Spectroscopic analysis of curing drying oils. *J Am Oil Chem Soc* 76(8):967–976
- Mallégol J, Gardette J-L, Lemaire J (2000a) Long-term behavior of oil-based varnishes and paints. Fate of hydroperoxides in drying oils. *J Am Oil Chem Soc* 77(3):249–255
- Mallégol J, Gardette J-L, Lemaire J (2000b) Drier influence on the curing of linseed oil. *Prog Org Coat* 39:107–113
- Mallégol J, Gardette J-L, Lemaire J (2000c) Long-term behavior of oil-based varnishes and paints. Photo- and thermooxidation of cured linseed oil. *J Am Oil Chem Soc* 77(3):257–263
- Meilunas RJ, Bentsen JG, Steinberg A (1990) Analysis of aged paint binders by FTIR spectroscopy. *Stud Conserv* 35(1):33–51
- Morley-Smith CT (1957) Metal-drier catalysis. *J Oil Colour Chem Assoc* 40:1035–1050
- Muizebelt WJ (1978) Oxidative crosslinking of alkyd resins studied with mass spectrometry and NMR using model compounds. *J Coat Technol* 70:83–93
- Richardson T, Korycka-Dahl D (1984) Lipid oxidation. In: Fox FP (ed) *Developments in dairy chemistry, vol 2, Developments series*. Applied Science Publishing, London, pp 241–263
- Schieberle P, Grosch W, Firl J (1984) Photolysis of unsaturated fatty acid hydroperoxides. In: Bors W, Saran M, Tait D, Gruyter D (eds) *Proceedings of the third international conference on oxygen radicals in chemistry and biology*, Berlin, 1984
- Socrates G (2004) *Infrared characteristic group frequencies – tables and charts*, 3rd edn. Wiley, West Sussex
- Van den Berg JDJ (2002) *Analytical chemical studies on traditional linseed oil paints*. Academic Proefschrift – PhD thesis, Universiteit Amsterdam
- Van den Berg JDJ, Van den Berg KJ, Boon JJ (1999) Chemical changes in curing and ageing oil paints. In: Bridgeland J, Brown J (eds) *ICOM-CC, 12th triennial meeting*. James & James, London, pp 248–253
- White WB (1974) The carbonate minerals. In: Farmer VC (ed) *The infrared spectra of minerals, vol 4, Mineralogical society monograph*. Bartholomew Press Dorking, Surrey, pp 227–284
- Wilhelm C, Gardette J-L (1994) Infrared identification of carboxylic acids formed in polymer photooxidation. *J Appl Polym Sci* 51:1411–1420
- Zumbühl S, Scherrer N, Ferreira E, Hons S, Müller M, Kühnen R, Navi P (2011) Accelerated ageing of drying oil paint – an FTIR study on the chemical alteration. *Zeitschrift für Kunsttechnologie und Konservierung* 25(2):139–151
- Zumbühl S, Scherrer NC, Eggenberger U (2014) Derivatization technique to increase the spectral selectivity of 2D FTIR-FPA imaging – analysis of binder composition in aged oil and tempera paint. *Applied spectroscopy* 68(4):458–465